THE CATALYTIC OXIDATION OF ORGANIC COMPOUNDS IN THE VAPOR PHASE

BY

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GENERAL INTRODUCTION

American Chemical Society Series of Scientific and Technologic Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in coöperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical development. The American Chemical Society named as Trustees, to make the necessary arrangements for the publication of the monographs, Charles L. Parsons, Secretary of the American Chemical Society, Washington, D. C.; John E. Teeple, Treasurer of the American Chemical Society, New York City; and Professor Gellert Alleman of Swarthmore College. The Trustees have arranged for the publication of the American Chemical Society series of (a) Scientific and (b) Technologic Monographs by the Chemical Catalog Company of New York City.

The Council, acting through the Committee on National Policy of the American Chemical Society, appointed the editors, named at the close of this introduction, to have charge of securing authors, and of considering critically the manuscripts prepared. The editors of each series will endeavor to select topics which are of current interest and authors who are recognized as authorities in their respective fields. The list of monographs thus far secured appears in the publisher's own announcement elsewhere in this volume.

The development of knowledge in all branches of science, and especially in chemistry, has been so rapid during the last fifty years and the fields covered by this development have been so varied that it is difficult for any individual to keep in touch with

the progress in branches of science outside his own specialty. In spite of the facilities for the examination of the literature given by Chemical Abstracts and such compendia as Beilstein's Handbuch der Organischen Chemie, Richter's Lexikon, Ostwald's Lehrbuch der Allgemeinen Chemie, Abegg's and Gmelin-Kraut's Handbuch der Anorganischen Chemie and the English and French Dictionaries of Chemistry, it often takes a great deal of time to coördinate the knowledge available upon a single topic. Consequently when men who have spent years in the study of important subjects are willing to coördinate their knowledge and present it in concise, readable form, they perform a service of the highest value to their fellow chemists.

It was with a clear recognition of the usefulness of reviews of this character that a Committee of the American Chemical Society recommended the publication of the two series of monographs under the auspices of the Society.

Two rather distinct purposes are to be served by these monographs. The first purpose, whose fulfilment will probably render to chemists in general the most important service, is to present the knowledge available upon the chosen topic in a readable form, intelligible to those whose activities may be along a wholly different line. Many chemists fail to realize how closely their investigations may be connected with other work which on the surface appears far afield from their own. These monographs will enable such men to form closer contact with the work of chemists in other lines of research. The second purpose is to promote research in the branch of science covered by the monograph, by furnishing a well digested survey of the progress already made in that field and by pointing out directions in which investigation needs to be extended. To facilitate the attainment of this purpose, it is intended to include extended references to the literature, which will enable anyone interested to follow up the subject in more detail. If the literature is so voluminous that a complete bibliography is impracticable, a critical selection will be made of those papers which are most important.

The publication of these books marks a distinct departure in the policy of the American Chemical Society inasmuch as it is a serious attempt to found an American chemical literature without primary regard to commercial considerations. The success of the venture will depend in large part upon the measure of coöperation which can be secured in the preparation of books

dealing adequately with topics of general interest; it is earnestly hoped, therefore, that every member of the various organizations in the chemical and allied industries will recognize the importance of the enterprise and take sufficient interest to justify it.

AMERICAN CHEMICAL SOCIETY

Preface

When—because of the prodigality of his brother, Epimetheus, in bestowing upon the animals of his creation all of the splendid gifts of the gods—Prometheus had no worthy blessing to give his master work, man, he ascended to heaven, lighted his torch at the chariot of the sun, and brought down fire. With fire man could then conquer the earth and mold it to his use.

Other than in mythology and in the imagination of erstwhile historians, we have no intimation of the origin of fire on the earth. However, man's own record shows that for many thousands of years he knew and used fire, and the progress of civilization may be measured in terms expressing the extent to which fire has been used. The oldest writings of India taught that fire was one of the elements, and the history of alchemy teems with speculations on its cause and use. Long ages passed before the empirical knowledge of primitive man and the speculations of the alchemists were woven with scientific observations into a credible theory and explanation of fire, combustion, and oxidation.

Although oxidation is one of the commonest reactions known and is widely used as a source of energy, it is only within the past fifty or sixty decades that concerted efforts have been made to study individual reactions systematically and to apply them in the formulation of useful processes. It is only natural that the effect of catalysts should have received early attention, and it is worthy of note that some of the earliest observations of catalytic effects had to do with oxidation reactions. In some cases development has been rapid and industrial processes have been worked out; in other cases, troublesome obstacles have been encountered and development delayed.

It has been the purpose of the authors to consider the facts regarding both developed and undeveloped processes and to review these critically in so far as possible. The subject could have been approached from several angles but it was believed that a consideration of the reactions involved and products formed constituted the most satisfactory method of treatment for the present purpose. This method of approach has made it possible to show to better advantage the effects of different catalysts on the various individual reactions and to classify the catalysts according to activity and directive power. A consideration of catalyzed decomposition reactions has been necessary in the case of aliphatic compounds because such reactions are of great importance in the oxidation processes.

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The various reactions have been carried through historic sequences from laboratory scale experiments to technical developments wherever possible. When sufficient data were available, industrial practice has been discussed. In many cases, the discussion could not be made as critical as desired because trade secrecy prevented the use of industrial data as illustrative material, because the multiplicity of conditions used in vapor phase oxidations made adequate comparisons and confirmations impossible, and because the paucity of data, published or otherwise, made it difficult to obtain sufficient knowledge of certain reactions. Nevertheless, a large amount of information has been gleaned from the scattered literature and arranged according to the scheme already mentioned.

It has been necessary in some cases to make free use of the patent literature because of the scarcity of other sources of information. This is an unsatisfactory solution because of the recognized unreliability of the patent literature relating to catalysts. Many patents are undoubtedly the result of sound observations and may be relied upon as sources of information; many, however, are crowded with claims that constitute wide extrapolations from any experimental evidence and, hence, are not to be relied upon as supports for theories and explanations. This uncertain nature has been recognized in the present use of the patent literature and patents have been depended upon principally to indicate the trend of activity in the various fields.

The authors are especially indebted to Mr. J. M. Weiss and Dr. C. R. Downs for having seen the possibility of a book on catalytic oxidation of organic compounds and for having instigated the present volume. They are also indebted to these men for critically reviewing the manuscript, especially those parts dealing with aromatic hydrocarbon oxidation, and for furnishing valuable information regarding industrial methods and apparatus. They gratefully acknowledge the aid of Prof. J. H. James and Mr. Chester E. Andrews in critically reviewing the entire manuscript.

L. F. M.
D. A. H.

Cambridge,
Massachusetts,
June, 1932.

Contents

Chapter I

Introduction—Catalysis

The fact that chemical action between two or more given compounds may be influenced by the presence of a relatively small quantity of an extraneous substance was recognized very early in the development of chemical theory, but the first generalization in regard to the nature of the forces which operate in such cases was made by Berzelius [1] in 1836 when for purposes of convenience he applied the term "catalytic force" to explain processes of this kind. Early studies in catalysis were limited almost exclusively to the action of platinum [2] although Dulong and Thenard [3] showed that gold, silver, and even glass, possess the same property at higher temperatures, and Faraday [4] carried on a detailed investigation regarding the power of metals and other solids to induce the combination of gases. The correlation of catalysis with the laws of chemical reaction velocity was made by Wilhelmy [5] as early as 1850 and his initial researches were later extended to a detailed study of the influence of changes in concentration, temperature and pressure by Lowenthal and Lennsen,[6] Berthelot,[7] Harcourt and Esson,[8] Warder,[9] Urech,[10] Van't Hoff, Arrhenius, and many others.

The potentialities of the application of catalytic methods in industry were foreseen by Ostwald [11] when he prophesied that a scientific knowledge and control of catalytic phenomena would lead to immeasurable results technically. This prophecy has been fulfilled in a large measure, and today the problems associated with catalysis are recognized as being of far reaching and fundamental importance to the chemist. Catalytic effects are present in even the most ordinary operations. Frequently, processes eminently successful in laboratory glass apparatus are doomed to failure when transferred to the plant with its iron, steel, or copper equipment simply because of some catalytic effect of the container wall. On the other hand, processes which a few years ago were considered laboratory curi-

[1] *Jahresber.* 15, 237 (1836); *Ann. chim.* (III) 61, 146 (1836).
[2] Döbereiner, *Schweigger's Jl.* 34, 91 (1822); 38, 321 (1823); *also* Turner, *Edin. Phil. Jl.* 11, 99 and 311 (1834) and Davy, *Phil. Trans.* 97, 45 (1817).
[3] *Ann. chim.* (II) 23, 440; 24, 380 (1823).
[4] Faraday, *Phil. Trans.* 114, 55 (1834).
[5] *Pogg. Ann.* 81, 413, 499 (1850).
[6] *J. prakt. Chem.* (i) 85, 321, 401 (1862).
[7] *Compt. rend.* 59, 616 (1864); *Ann. chim.* (iv) 18, 146 (1869).
[8] *Phil. Trans.* 167, 117 (1867).
[9] *Am. Chem. J.* 3, 203 (1881).
[10] *Ber.* 16, 762 (1886); 17, 2165 (1884); 20, 1836 (1887).
[11] Ostwald, *Z. Elektrochem.* 1, 995 (1901).

osities or even impossibilities are today being operated on a tremendous scale with the aid of catalysts. As examples of these one may point to the synthetic ammonia industry, the synthetic methanol industry, and the rapidly expanding development of the hydrogenation of coal and oil.

Although it was early recognized that application of pressure to the system

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$
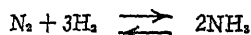
would give a favorable conversion at elevated temperatures it was not until Haber applied the theoretical generalizations of catalysis to the process that it was possible to obtain reaction rates of sufficient velocity to make the synthesis a commercial success. In this instance pressure offsets the effect of temperature but it would require enormous pressures to give favorable equilibrium conditions at the temperatures necessary to obtain reaction in the absence of catalysts. The use of catalysts permits operation at lower temperatures and hence, at lower pressures, which is equivalent to saying that a catalyst is a substitute for high temperatures.

The present study of this very complicated subject aims to present types of oxidation processes in which a catalyst has been found to play an important rôle. In general, the various theories as to the mechanism of catalysis will not be considered except for a few introductory remarks. The discussion will be limited in the case of each of the reactions studied to the development of the given chemical transformation under different conditions, to industrial application, or to the point where the highest yields have been obtained. In every instance this development has been accompanied by the perfection of the necessary apparatus and mechanical devices. It has been slow, often proceeding tediously as the result of the efforts of many investigators and stretching over a considerable period of time. For this reason, the development may often be followed to advantage by indicating the historical sequences.

Controlled or directed oxidation is of great technical importance. Especially in the field of hydrocarbon oxidation, where a great number of side reactions are possible, it is essential that selective catalysts be found. The discovery of a catalyst capable of directing the oxidation of such hydrocarbons as are found in natural or refinery waste gases to formaldehyde alone without at the same time accelerating the oxidation of this compound to waste products would be extremely valuable, since the availability of very cheap formaldehyde would make possible cheap synthetic resins having such unique uses as in the manufacture of furniture or automobile bodies.

In the case of hydrocarbon oxidation the spread in value between the hydrocarbon raw material and the possible products is generally so large that relatively small yields may be economically exploited. Formaldehyde admixed with acetaldehyde and some methanol and obtained in the removal of oxygen from natural gas before transmission over long distance lines to

prevent corrosion is finding its way on the market.* A more general practice of this oxygen removal would result in making available large quantities of formaldehyde, especially as the natural gas industry increases in size. This production of formaldehyde is largely a matter of economic balance, however, and its net worth will determine the extent of its production.

The definition of certain general terms is necessary before proceeding to a more detailed discussion. A *catalyst* is a substance which in minimal amounts will bring about the transformation of large quantities of the reacting substances and which will be found unchanged in its chemical composition at the end of the reaction. This does not imply that the physical state of the catalyst remains unaltered, since it is known, for example, that platinum wire or gauze actually does change during the process of catalytic oxidation, becoming pitted or spongy and presenting a grayish appearance under the microscope. A catalyst is generally supposed to modify the velocity of two inverse reactions to the same degree and, therefore, does not affect the final state of equilibrium in any given chemical system. In other words, the state of equilibrium is independent of the nature and quantity of the catalyst. The modification or the initiation of a reaction by a catalyst is referred to as *positive catalysis* when the reaction velocity is accelerated. When the reaction itself develops substances which themselves accelerate the reaction, the process is referred to as *auto-catalytic*. *Promoters* are substances which by admixture with the catalyst enhance its positive catalytic effect. For example, iron, nickel and cobalt (or their oxides) frequently show a marked increase in their catalytic action in the presence of the oxides of chromium, thorium, uranium, beryllium, antimony, etc. In general, the promoter differs considerably from the catalyst in respect to valence, chemical basicity, ease of reduction, etc. Such a mixture is usually prepared by the evaporation of a solution of definite concentration of salts such as nitrates, acetates, etc. These are frequently deposited upon a suitable base and then treated in such a way as to insure a deposit of either the metals or their oxides in finely divided condition. The terms *negative catalysis* (or *retardation*) and *auto-retardation* may be readily understood as denoting the reverse of the processes which have just been defined. Catalytic *poisons* are substances which reduce the activity of solid catalysts. Investigation alone can determine the extent to which a given catalyst may be *activated* or *poisoned* by the presence of other substances. *Carriers* is a term which is used to designate materials either of a porous nature, such as unglazed porcelain, pumice, charcoal, asbestos masses, alundum, infusorial earth, etc. which when impregnated with the catalyst afford it a greater surface per unit of bulk; or of compact surfaces, such as that afforded by iron pellets, granulated aluminum, etc. on which a catalyst is plated or deposited. Material employed in this way should be free from impurities which might poison

* *Compare* Chapter VI.

the catalyst, should be incapable of chemical reactions with the catalyst and, if possible, be positively (though weakly) catalytic to the reaction in which it is to be employed. *Contact mass* is a term which is used to designate such combinations of the active substance with the carrier as actually function in the process of catalysis.

In practice it is customary to express the capacity of a given system in terms of *space velocity*, which is defined as the volume of reacting gas, measured at normal temperature and pressure, passed in contact with one volume of catalyst per hour. In a given system as the space velocity is increased from zero, the conversion to products, starting from the equilibrium value, begins to fall off until when the space velocity reaches a very
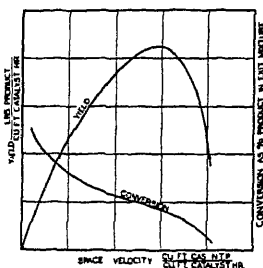

high value, the conversion may be quite small, due to the decreased time of contact of reactants with the catalyst. At the same time, however, the yield per unit time, i.e. the product of the space velocity and the conversion, rises from a low value, passes through a maximum and then decreases. When the space velocity is low, the conversion may be at or near equilibrium and yet only low yields result. Even under experimental conditions the final approach to equilibrium is so slow that it is often necessary to make the approach from both sides of the reaction in independent experiments in order that no uncertainty may exist as to the final state. If,

Fig. 1.—Effect of space velocity on conversion and yield in the case of a heterogeneous reaction.

as the space velocity is increased, the conversion is not markedly affected at first, a condition frequently met with, the yield rises somewhat in proportion to the amount of material treated per unit time. Then, unless the reaction rate is very rapid, the conversion may decrease with increase in velocity of reactants through the catalyst faster than is proportional to space velocity increase. In such a case the yield begins to decrease as more material is treated per unit time. Obviously, unless the reaction rate is infinitely rapid, the conversion approaches zero as the space velocity approaches a large value and the yield consequently approaches zero under such conditions. Thus, in actual operation it is usually the practice to be content with conversions less than equilibrium in order to obtain high yields. At the same time the extent of reaction and amount of material capable of treatment per unit time depends upon the capacity of the equipment to add or remove heat. The power required to circulate the gases through the catalyst increases rapidly as the space velocity is increased, due to the increased skin friction at the catalyst surface, and is a factor to be considered industrially. On the whole, the determination of the proper space velocity to use with a given reaction and equipment is a complex problem in economic balance dependent on a number of variables, too involved for discussion here.

The functions which a catalyst may perform depend upon the nature and complexity of the reactions involved. These functions may be broadly grouped under two headings: (1) to increase the rate of a given reaction or, as is usually the case, to lower the temperature at which a reaction will occur at a desirable rate, and (2) to direct a reaction along a particular path when several are possible. The distinction between these two functions is not sharp since it is quite possible for a catalyst to do both. Thus, a selective catalyst is ordinarily one that increases the reaction rate as well as directs the reaction. Industrially, both of these functions are important since it is not only desirable to obtain high yields of a pure product but also to obtain high yields rapidly. In numerous cases, however, the selection of a catalyst for a given process or reaction may depend only on its ability to perform one or the other of these functions, so that it is justifiable to discuss these functions more or less separately.

The energy contribution of a catalyst to a reacting chemical system is zero, since the catalyst emerges from the reaction without loss or chemical change and is capable of inducing changes in an indefinite quantity of reacting materials. It follows from this that a catalyst can cause no change in a chemical equilibrium, otherwise the introduction of a catalyst could be used to shift the equilibrium in either direction and thus by alternately introducing and removing the catalyst to set up a sort of perpetual motion, an impossibility.[12] The final state of equilibrium of a reversible reaction depends only upon the ratio of the velocities of the two inverse reactions and since this final state remains unaltered by the introduction of a catalyst, it may be deduced that the catalyst affects the two reaction velocities to the same extent in order to keep their ratio constant. Also, since the final state of equilibrium is independent of the catalyst, it may be observed that the state of equilibrium is independent of both the reaction and the quantity of the catalyst. Thus, in the case of the contact process for sulfuric acid manufacture, it is not the equilibrium, but only the velocity of its attainment which is affected by the use of vanadium pentoxide or iron oxide in place of platinum.

It should be quite obvious, then, that if the catalyst is markedly altered in its physical or chemical nature by a reaction occurring in its presence, the equilibrium of the reaction would not be independent of the catalyst particularly if the ratio of catalyst to reactants is large. However, if the term catalyst be so defined and understood as to preclude such alterations in character or at least to confine the alterations to relatively small changes in an insignificant amount of material compared to the reacting substances, then it is possible to ignore any possible effect of the catalyst on the equilibrium of a system.

Actually, due to the fact that other influences are present, these theoretical criteria are not strictly adhered to. Because of side reactions occurring at the same time as the main reaction and involving the catalytic material,

[12] *Cf.* Van't Hoff, "Lectures on Theoretical Physical Chemistry," 1898, p. 215.

the catalyst may not emerge from the system without loss or chemical change. Because of the accumulation of poisons at the catalyst surface due to impurities present in the reactants or formed by side reactions, the catalyst may not be capable of inducing changes in an indefinite quantity of material. The practical limitations make it necessary that the catalysts be renewed or reactivated periodically, often at considerable trouble and expense.

The generalization that a catalyst does not affect the equilibrium of a reversible system and must, hence, influence the rate of both forward and reverse reactions equally has not only been substantiated experimentally but has been used in the selection of proper catalysts for a given reaction. Thus, Lemoine [13] demonstrated completely that in the reversible system

$$H_2 + I_2 \rightleftharpoons 2HI$$
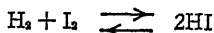
for all temperatures, the same point of equilibrium was reached from both directions, when a catalyst such as platinum was used.

In searching for catalysts good use has been made of the fact that catalysts affect both the forward and reverse reaction rates. The reverse reaction of the one desired is tested over different catalysts and the character and amount of the decomposition products noted. The catalyst giving the desired reverse reaction at a suitable rate is then chosen for use in studying the forward reaction. This procedure is especially valuable in studying catalysts for reactions to be conducted under pressure since it is far simpler and more rapid to make decomposition experiments at atmospheric pressure than synthesis experiments under high pressure. That this expedient is of considerable industrial utility may well be, since, according to Patart, the isolated experiments of Sabatier on catalytic decomposition of methanol served as a guide in the search for contact substances for the synthesis of the alcohol. The experimental utility of the scheme has been demonstrated in the numerous publications that have appeared recently in regard to the high pressure synthesis of various organic compounds from mixed gases.

Sabatier and Mailhe [14] showed that the route over which a reaction could be made to occur depended upon the presence of certain catalysts. Thus, ethanol decomposes in two ways:

$$C_2H_5OH = C_2H_4 + H_2O$$
$$C_2H_5OH = CH_3.CHO + H_2$$
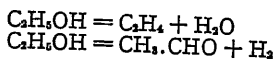
With thoria as a catalyst the first reaction takes place almost exclusively; with silver or copper, the second occurs practically alone; and with most catalysts both occur simultaneously. This apparent ability of a catalyst to direct a reaction over a certain route is due to the selective influence in accelerating the rate at which a single reaction of a number of possible ones, occurs. In no case are the equilibrium conditions affected.

[13] Ann. chim. phys. (5), 12, 145 (1877).
[14] Ann. chim. phys. (8) 20, 341 (1910).

The influence of catalysts in affecting the route of the alcohol decomposition reaction is intimately associated with the ability of the catalysts to adsorb selectively hydrogen or water vapor. When passed over such catalysts as reduced nickel, copper, or iron, materials known to promote other hydrogenation and dehydrogenation reactions and to adsorb hydrogen strongly, the alcohol is almost quantitatively broken down to aldehyde and hydrogen. When passed over alumina or thoria, the alcohol decomposes exclusively to olefin and water. The conclusion, then, is that such catalysts must adsorb water vapor very strongly. It has indeed been shown [15] that alumina will retain a certain proportion of water even after prolonged exposure to phosphorous pentoxide, which has a very high affinity for water, thus showing that it, at least, fits the explanation. Catalysts such as titania, on the other hand, affect the alcohol decomposition in such a way that both of the reactions occur and both aldehyde and olefin are formed. However, the relative proportions of the two reactions may be controlled to some extent over this catalyst. Thus, by using aqueous ethanol the reaction giving olefin and water is suppressed in favor of the dehydrogenation reaction and by using hydrogen with the alcohol vapor the dehydration reaction is favored.[16] These results do not mean that the equilibria in the system are in any way affected but that the relative rates of the two reactions are so changed as to give the variant results.

This ability of certain catalysts to increase the reaction rate of one reaction without influencing the rates of other possible ones has made it possible to synthesize practically pure methanol from mixtures of hydrogen and carbon monoxide. Although it was early shown that a great variety of aliphatic compounds could be synthesized from mixtures of hydrogen and carbon monoxide, the results obtained were of no practical significance since very complicated mixtures, impossible to separate, were produced. However, the extensive researches of Patart and the Badische Anilin u. Soda Fabrik soon showed that it was possible to use catalysts of sufficient selectivity to enable the production of pure methanol to become an economic possibility. The same is true of mixtures of carbon dioxide and hydrogen and today enormous quantities of pure methanol are being manufactured at a very low price from both mixtures. The work at present has taken on another aspect, the synthesis of alcohols higher than methanol from the same mixtures, a reaction requiring still greater selectivity on the part of the catalysts used.[17]

Although the simplest and most commonly recognized effect of catalysts is to accelerate the rate of a chemical change or exert positive catalysis, it is possible in certain instances for a catalyst to retard a reaction or exert a negative effect. Negative catalysis should be distinguished from the inhibition of positive catalysis brought about by the action of poisons which

[15] Johnson, *J. Am. Chem. Soc.* **34**, 911 (1912).
[16] Bancroft, *J. Phys. Chem.* **21**, 591 (1917).
[17] In this regard note that higher alcohols have actually been manufactured for a number of years on an industrial scale from mixtures of hydrogen and carbon monoxide. Crane, *Ind. Eng. Chem.* **22**, 799 (1930).

destroy the normal activity of a positive catalyst, since it is an entirely distinct effect, independent of any incidental influences. This term, negative catalysis, is somewhat misleading as has been pointed out in connection with oxidation reactions. Moureu and Dufraisse [18] prefer to speak of anti-oxygenic activity, since, as they point out, the use of the word "negative" applied to catalysis might lead to the obvious misunderstanding that a catalyst was able to reverse the course of an otherwise spontaneous reaction, which it is not capable of doing. Numerous examples of this negative or retarding effect may be found and the effect divided into groups as with positive catalysis: a definite decrease in reaction rate, and an accelerated decrease in reaction rate (auto-retardation). The principle of negative catalysis has found most widespread use in vapor phase reactions in the suppression of detonations which occur under certain conditions of operation of internal combustion engines.

The simplest explanation possible for this phenomenon is based on the assumption that the negative catalyst combines with one or more of the substances involved in the reaction, and in this way decreases its effective concentration. While some experimental evidence has been advanced to support this theory, some of the existing facts seem to indicate a more complex mechanism. Thus, Moureu and Dufraisse [18] in determining the inhibiting action of certain compounds toward the oxidation of benzaldehyde, acrolein, etc. found that virtually no oxidation of the vapors occurred, notwithstanding that they were saturated with oxygen and contained none of the inhibitor, which had a very low vapor pressure and was present in only minute amounts in the liquid. It is difficult to account for this inhibiting action on the basis of removal of one of the reactants from the field of reaction since enormous excesses of both must have existed. The recognition of these negative effects has considerably broadened the field of catalysis but has at the same time further complicated the problem of explaining the fundamental mechanism. To give examples here of the results obtained by numerous workers would lead too far, particularly as it is only desired to give some idea of the general trend.

A theory that an intermediate compound, which is not reactive under the conditions of the reaction, forms between the catalyst and the reactants has been proposed by Taylor [19] and Underwood [20] as an explanation for negative catalysis. The idea of chain reactions has also been advanced [21] as an explanation. In this case, the negative catalyst functions by absorbing the energy of the active molecules and thus breaking the reaction chain.

It has been found that in certain instances mixtures with one constituent present in preponderance have a much greater catalytic activity than any of the components of the mixture taken singly and greater than may be accounted for on the basis of an additive effect. This action has been

[18] Chem. Rev. 3, 113 (1926).
[19] J. Phys. Chem. 27, 322 (1923).
[20] Proc. Natl. Acad. Sci. 11, 78 (1925).
[21] a. Christiansen, J. Phys. Chem. 28, 145 (1924); b. Weigert and Kellermann, Z. Elektrochem. 28, 456 (1922).

termed promotion and is directly opposed to the action of poisoning since it represents the activation of the catalyst. Although innumerable examples of the effect exist, no satisfactory explanation has been offered to show the mechanism. The X-ray study of catalysts composed of mixtures should furnish a fertile field for investigation of this extremely interesting and complicated subject.[22]

To review completely the numerous examples of promoted catalysts, most of which are mentioned in the patent literature, would be entirely out of place here. It is, however, interesting to note that the term was used and the effect noticed early in the industrialization of the water gas reaction.[23] Additions of the oxide of chromium, thorium, uranium, beryllium, and antimony to the nickel, iron, or cobalt catalysts was found to increase greatly the activity of these materials toward this reaction.[24]

From a study of the mechanism of the poisoning action of water vapors and oxygen on iron ammonia catalysts [25] and by making certain assumptions, Almquist [26] has been able to calculate that in pure iron catalysts about one atom in two thousand is active toward ammonia synthesis, whereas in iron catalysts promoted by alumina about one atom in two hundred is active. This shows the remarkable added activity obtainable by the use of promoters. That the effect is complicated beyond any simple explanation is evidenced further by some of the results of Almquist and Black. These workers have shown that whereas an iron-alumina catalyst shows greater activity toward ammonia synthesis at atmospheric pressure than an iron catalyst containing both alumina and potassium oxide, the latter catalyst is 50 per cent more active when the pressure is raised to 100 atmospheres.

The presence of small amounts of certain materials in the reacting gases can completely destroy the activity of a catalyst. Certain side reactions occurring along with the main reaction may produce substances which deposit on the catalyst and destroy its usefulness. These effects are known as poisoning, and are of the utmost industrial importance since it is probable that the greater part of the replacement or revivication of catalysts necessary in industrial operation is made so by the action of minute traces of poisons contained in the reacting materials. It was not until the discovery of the effect of certain foreign materials, especially arsenic compounds, in destroying the life of the platinum catalysts that the contact method of sulfuric acid manufacture was industrially successful. Traces of water vapor rapidly reduce the activity of the promoted iron catalysts in the synthesis of ammonia; consequently the mixtures of hydrogen and nitrogen must be rigidly dried. Traces of the compounds of sulfur, selenium, tellurium, etc. in the mixtures of hydrogen and carbon monoxide made from low grade coals and used in the synthesis of methanol, poison

[22] See page 31 and Aborn and Davidson, *J. Phys. Chem.* **34**, 522-30 (1930).
[23] Brit. Pat. 19249 (1910) Badische Anilin u. Soda Fabrik.
[24] Brit. Pat. 27963 (1913) Badische Anilin u. Soda Fabrik.
[25] Almquist and Black, *J. Am. Chem. Soc.* **48**, 2814 (1926).
[26] Almquist, *J. Am. Chem. Soc.* **48**, 2820 (1926).

the metallic oxide catalysts very rapidly. The extensive literature on the action of poisons and methods used to combat their effect, contained largely in patents, indicates two methods of approach to the solution of the problem. One of these, the strict purification of reactants and catalytic material, is of most immediate benefit and the only way out in some instances. Considerable progress, however, has been made in the development of catalysts resistant to the specific poisons that it is necessary to tolerate in industrial applications. In general, the more active catalysts are the most sensitive to poisons and the industrial trend has been toward the use of rugged catalysts with only moderate activity.

The mechanism of the poisoning action is somewhat obscure and probably varies with the catalysts as well as the poisons. In the case of the metalloid poisons a non-volatile compound is probably formed with the active catalyst points which destroys the activity. The activity of the metallic catalysts is probably destroyed by the formation of non-volatile, irreducible oxide films by traces of water vapor,[27] carbon oxides, oxygen, etc. present in the reaction mixtures. Catalysts used in reactions where a large amount of polymerization or condensation may occur between organic molecules are frequently smothered by layers of the polymerized mass. Overheating of the catalyst may cause a sintering effect, or semi-melting, especially of the active surface points which are as a result permitted to come closer in contact with the main body of catalyst atoms and thus to become more nearly saturated in valence with loss of activity. The oxide catalysts so successfully used in a number of oxidation processes are relatively free from many of the poisoning effects that so easily deteriorate the metallic catalysts. Sintering or fusion has even been found to improve the activity of the vanadium pentoxide catalysts; and the chief difficulty with foreign matter in the raw materials is contamination of product rather than destruction of catalyst activity. This apparently rugged nature of these oxide catalysts may in large part be due to the mechanism in which they are active, i.e. through a succession of reductions and oxidations.

The ability to express the effect of various factors mathematically is a distinct aid in studying a catalytic reaction and in determining the set of conditions which will give the best practical results and thus increase the commercial value of the process. The intelligent application of theoretical principles is, under these circumstances, extremely useful. It must be borne in mind, however, that only in rare cases can the suitability of a catalyst for a particular reaction be predicted on the basis of theoretical reasonings. Such predictions have been made successfully in cases where a given catalyst is known to accelerate a given reaction and it, therefore, has seemed reasonable to assume that under the proper combination of external forces the same catalyst might accelerate the reverse reaction. A notable illustration of this is to be found in the fact that the application of

[27] Emmett and Brunauer, *J. Am. Chem. Soc.* **52**, 2682 (1930).

iron and nickel as catalysts in the synthesis of ammonia from hydrogen and nitrogen, resulted from a consideration of the activity of these metals in promoting the decomposition of ammonia into its elements at high temperatures. In general, however, the only way to determine what catalyst to use to accelerate a given reaction is by the purely empirical method of trial and error. For example, the fact that vanadium oxide is known to be a good oxidizing catalyst, is of no specific assistance in determining the effect which it will produce upon a given hydrocarbon in the presence of air, the direction which the oxidation will take or the intermediate products which will be formed. The most direct way to arrive at conclusions in these matters is not by speculations which represent little more than guess work but by actually experimenting to see what happens. More often than not the results will be entirely new and unexpected. While the value of purely theoretical investigations, such as those on the absorptive powers of various catalysts for a component or product of a given reaction, cannot be questioned, it nevertheless seems probable that the same amount of time and effort might prove of more immediate industrial value if expended in determining exactly what happens to different chemical reactions under different sets of conditions. The accumulation of exact experimental data in the form of empirical facts must always precede the formulation of generalizations of any value. Each year new reactions of a catalytic nature are discovered which could not have been or at least were not predicted on the basis of any data previously known. It, therefore, seems reasonable to conclude that real aid to the advancement of a knowledge of the subject of catalysis will come principally through the accumulation of experimental data and not through speculations based on relatively meagre data which may be available.

The great majority of catalytic reactions which have been applied technically as industrial processes are those where solid catalytic material acts on gaseous material. They, therefore, represent one type of *heterogeneous* catalysis. In such cases, theoretical considerations, especially those based upon the laws of mass action, do not apply in the same way as in cases where the system is *homogeneous,* i.e. where the catalyst together with all of the components of the reaction are in the same state of aggregation as, for example, when all are either liquids or gases.

In cases of homogeneous catalysis, in which the catalyst remains in intimate mixture with the components of the reaction, it acts by its mass, and in many instances the value of the velocity coefficient varies in direct proportion to the concentration of the catalyst. For a comparison of the efficiency of different catalysts in such systems, values for velocity coefficients may be obtained which often provide an accurate basis for estimating the relative activity of the catalysts under question.

However, in the case of heterogeneous catalysis, i.e. where the catalyst is solid and cannot be in a condition of true admixture with the components of the reaction, it is impossible to apply reaction velocity formulae with the

same assurance. Careful study of cases of heterogeneous catalysis on quantitative lines has revealed the fact that other factors besides mass action are controlling. This has been very clearly and pointedly brought out by the experiments of Bone and Wheeler[28] on the combination of hydrogen and oxygen at hot surfaces.

These experiments were made by circulating mixtures of electrolytic hydrogen and oxygen over fragments of unglazed porcelain contained in a tube and maintained at constant temperature. As the reaction

$$2H_2 + O_2 = 2H_2O$$
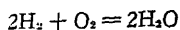
proceeded, the pressure fell regularly and provided a record of the change taking place. From this pressure change record it was possible to calculate the velocity of the reaction and the order. Since both hydrogen and oxygen disappear during the reaction, hydrogen twice as rapidly as oxygen, it might be expected that the reaction would show the characteristics of either a bi- or tri-molecular type. However, calculation of the velocity constants showed that the reaction was unimolecular in order. Experiments were then made in which hydrogen and oxygen were present in other than combining proportions and in which the partial pressures of each of the reactants as well as the total pressure was determined as the reaction progressed. A unimolecular constant calculated for the rate of disappearance of each reactant showed that the reaction was unimolecular with respect to hydrogen alone, i.e. the rate of change was proportional to the partial pressure of the hydrogen.

The results of this work have shown that the catalytic formation of steam from hydrogen and oxygen does not depend upon the ordinary mass action laws, but is an indirect process dependent upon a primary change at the catalyst surface involving hydrogen. Evidently the catalytic action of porcelain in this case is dependent upon some phenomena occurring at the surface and dependent upon the presence of hydrogen at that surface. It is probable that the interaction of oxygen with this "occluded" hydrogen is very rapid, perhaps instantaneous. Hence, in determining the reaction velocity of such heterogeneous reactions, the actual velocity of a chemical reaction is not being measured but rather a purely physical process, the rate at which hydrogen moves up to the surface and is activated. The operation of the law of mass action is completely masked since it is impossible to determine the concentrations of the reactants and products at the actual zone of interaction on the catalyst surface.*

It has been shown that the rate of heterogeneous reactions depends upon the rate at which the reacting components of a mixture can diffuse up to the surface of the catalyst, become activated, and react. Still another factor is involved, however, and this is the rate at which the product can

[28] Phil. Trans. Roy. Soc. 206 A, 1-75 (1906).
* It is interesting to note in the light of what has been said previously regarding speculations on catalytic processes that this series of experiments led directly to the development of surface combustion in England as an industrial process for generation of heat.

disengage and diffuse from the catalyst surface. This factor is of utmost importance since if the products of reaction were not removed from the active surface of the catalyst, it would become poisoned and further reaction would cease due to the impossibility of any reactant reaching the surface.

Nernst [29] considered that the equilibrium at the interface of two phases was established very rapidly, instantaneously compared to the rate of diffusion. The diffusion equation is similar in form to that of a monomolecular reaction and it is, hence, probable that measurement of the rate of heterogeneous reactions which appear to be monomolecular is really measurement of the rate of diffusion. Thus, heterogeneous reactions are determined as to rate by the velocity at which the reacting molecules can diffuse to the catalyst surface and penetrate or partly displace the adsorbed film. In the light of Langmuir's discoveries this view must be modified since not all of the surface may be active. The rate is then fixed by the rate of movement of reactants to active portions only of the catalyst and by the proportion of active surface present.

With a given reaction mixture and catalyst the rate of the heterogeneous reaction will be directly proportional to area of catalyst surface exposed. A homogeneous reaction by its very nature will be independent of surface area.[30] Contrary to what is true in the case of homogeneous reactions, the real order of heterogeneous reactions cannot be determined from the effect of pressure on the reaction velocity. Special conditions must be fulfilled which cannot be discussed here.[31]

From the very nature of heterogeneous catalysis it may be seen that the character of the surface of the material used as the catalyst is a very critical factor in determining the activity. Because of this sensitivity, it is difficult to reproduce catalysts in any desired condition of activity, a factor that has led to much dispute among experimental workers. Methods used in the preparation of the catalyst and the treatments given prior to use determine to a large extent the activity of a given material as a catalyst.

The porcelain surfaces used by Bone and Wheeler [28] in their combustion experiments were stimulated markedly in their activity by previous treatment with hydrogen and were reduced in activity by treatment with oxygen. The literature contains many other instances of where previous history has a marked influence on catalytic activity. Thus, finely divided metallic nickel varies greatly in activity depending upon its source and the temperature at which it is reduced. Nickel prepared by heating the nitrate and reducing the oxide formed during the heating is almost without catalytic activity toward the hydrogenation of vegetable oils. Reduction of the hydroxide prepared by precipitation from nickel sulfate gives a catalyst with considerable activity. Use of the nitrate rather than the sulfate re-

[29] Nernst, *Z. physik. Chem.* **47**, 52 (1904).
[30] Refer to Hinshelwood. "Homogeneous Reactions," *Chemical Reviews* **3**, (1926).
[31] For a discussion *see* Hinshelwood, "The Kinetics of Chemical Changes in Gaseous Systems," 1926, p. 125; Oxford, Clarendon Press.

sults in a catalyst of great activity. Ignition of nickel carbonate at 400° to 450° C. followed by reduction at 400° C. gives a poor catalyst whereas ignition and reduction at 250° to 300° C. results in a highly active catalyst. The sheet metal is practically devoid of catalytic activity.

Silica is also very characteristic in its action as a catalyst. Moderately calcined, precipitated silica dehydrates ethanol to ethylene at 280° C. When calcined at a higher temperature the silica does not decompose the alcohol until a higher temperature is reached and then the decomposition is partly dehydrogenation and partly dehydration. Pulverized quartz is still less selective in its action, causing the decomposition of ethanol to occur by dehydration and dehydrogenation at equal rates. In considering these various catalytic activities of silica, the striking variety of forms in which silica may exist must be considered. Silica formed by the addition of acid to sodium silicate or by the passage of silicon fluoride vapors into water is micro-amorphous in character, i.e. the atomic structure does not follow any regular order. In a general way the properties of this modification of silica resemble those of very finely ground vitreous silica. This has been shown by the use of X-ray powder photographs. Silica as quartz is stable up to 870° C. ± 10°. Above this temperature and up to 1470° C. ± 10° the stable form of silica is tridymite. From this temperature and up to 1710° C., the melting point, cristobalite is the stable form. All of these temperatures are based on atmospheric pressure conditions and constant and uniform temperatures.* It is unfortunate that the nomenclature applied to the various forms of silica, such as quartz, did not become standardized until after much of the experimental work with it had been done. As a result, uncertainty regarding the actual forms used as catalysts prevents clear cut comparisons to be made between the catalytic effects and the structure.

In the atmospheric pressure synthesis of hydrocarbons from hydrogen and carbon monoxide, Elvins [32] showed experimentally that reduced unsupported catalysts of cobalt, copper, or manganese prepared by ignition of the nitrates gave much greater conversions than the reduced precipitated oxides.

In practice, catalysts are frequently used in the form of a thin film on the surface of some more or less inert support. In this way it is possible to obtain granular catalysts having considerable physical strength, presenting a large exposure of surface, and necessitating the use of only minimum amounts of active material, which is frequently expensive.

Other and quite noticeable effects are also obtained in the activity of the catalyst by the use of certain supporting materials. Thus, a nickel catalyst supported on alumina is subjected to an effect similar to that of a protective colloid or a colloidal sol in that the reduced nickel is able to withstand higher temperatures without sintering or loss in activity and

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* For further details about silica *consult*. Sosman, "The Properties of Silica." A.C.S. Monograph No. 37. The Chemical Catalog Co. (1927).
[32] Elvins, *J. Soc. Chem. Ind.* 46, 473T (1927).

usually has an enhanced activity compared to that of an unsupported mass of metal. It is possible that the individual active points of the nickel are separated from each other in such a way by the molecules of the irreducible support that the tendency of the active atoms to cohere due to the effect of high temperatures is to some extent prevented, and the active atoms permitted to function as catalysts for a longer period of operation than is ordinarily possible. The same is true of the iron-aluminum oxide catalysts used in ammonia synthesis.

Many of the industrial vapor phase catalytic processes, especially those involving oxidation reactions, are decidedly exothermic in character and must be conducted within rather narrow temperature ranges for optimum results. Since reaction occurs at the surface of the catalyst in these instances, the heat evolved is liberated in a restricted zone at the very surface of the catalyst, and causes the temperature here to rise considerably above that which may be recorded by instruments in the catalyst mass or on the surface of the reaction vessel. To moderate this abnormal temperature rise, and, hence, to prevent the improper and undesirable reactions from occurring as well as to prolong the life of the active material, attempts have been made to use catalyst supports of good heat conducting material. To this end the catalyst is spread in a thin layer on the surface of metallic balls, turnings, or granules with the hope that the heat will be conducted away rapidly from the seat of the reaction, the catalyst surface. While this expedient is of considerable benefit in maintaining a more uniform temperature distribution in the individual catalyst particles, it does not insure the rapid conduction of heat from the center of the catalyst mass to the walls of the reaction chamber since thermal contact between the individual metal particles is usually poor because of the point type of contact between them. For this reason the expected results of good heat conduction have not always been realized by the use of metallic supports, especially where tubular reaction chambers of relatively large diameter have been used. Where small diameter catalyst-containing reaction tubes are used and the heat generated in the reaction has but a short distance to travel before it is dissipated from the tube wall, it is possible that decided improvement in operation will result from the use of good heat-conducting catalysts.

Numerous types of non-metallic supports are used and the catalyst added by soaking the granulated supporting material in a solution of the catalytic substance, by spraying on a solution containing the catalyst, by spreading on a paste or by simultaneously or consecutively precipitating the catalyst material together with a difficultly soluble carrier. This latter procedure permits of a more uniform distribution of catalyst over the carrier as well as a better control of the catalyst concentration relative to the support. The use of solid, porous granules, however, has the advantage in that only the surface need contain the active material, a point of considerable importance when such expensive catalysts as platinum,

osmium, ruthenium, and others are to be used. Although practically all of the inert supporting materials are bad heat conductors, they have other virtues which warrant their use. Thus, some are chosen primarily for resistance to high temperatures and good physical strength, others are chosen for their extreme porosity and hence, large surface, still others are used for their protective action in prolonging the life of the active material. These substances may range from broken fire-brick and pumice, to porous materials such as kieselguhr, silica gel, and active carbon, to protective materials such as alumina or magnesia. Asbestos makes an excellent carrier on account of its bulky nature and hence, very extended surface per unit of weight. On the other hand, it has the disadvantage of packing together under relatively small pressures and hence, of requiring use in thin layers.

Special consideration must be given to physical characteristics in the choice of catalyst support. Since asbestos fibers are not porous to any extent, catalysts supported on asbestos are held in the inter-fibrilar spaces. When asbestos is used, precautions must be taken to prevent the felt-like mass from compacting and increasing the resistance to gas flow. For this purpose, asbestos-supported catalysts are used in numerous thin layers, each layer on a separate perforated plate. Despite its resistance to temperature effects, asbestos is not favored as a support and the more rigid materials preferred.

Infusorial earth, a compacted mass of siliceous fossils deposited by sedimentation processes, presents unique characteristics. It has a very high, useful porosity due to the enormous numbers of inter-fossil spaces. During calcination of the silica fossils some of the porosity may be destroyed but the calcined material still possesses a very high degree of porosity. The surface exposure is enormous due to the flake-like structure of the porous individual fossil shapes. This material may be used as a support in a number of different ways. The earth may be moistened, molded by pressure into various shapes, calcined for increased strength, and then impregnated with the catalyst. The catalyst may be mixed with the disintegrated earth and the whole molded or formed into granules. For liquid reactions, such as the hydrogenation of vegetable oils, the catalyst may be deposited on the disintegrated earth particles and used as a suspension.

In the case of porous catalyst carriers, impregnated throughout with active catalytic material, the catalyst within the pores of the individual granules is at least partly effective. The increased catalyst exposure thus obtained comprises one of the advantages of porous carriers. The relative effectiveness of the catalyst in the interior pores is, of course, dependent upon the rate at which the reactants can reach it, the rate at which the products can leave, and the velocity at which the reactants pass over the catalyst mass. With slow gas rates the "interior" catalyst can be more effective, whereas with high gas rates the proportion of reaction which occurs within the pores is diminished. However, the longer exposure of reactants to catalyst possible in the pores may have a detrimental effect in

certain reactions where secondary reactions, requiring a longer time for completion, may result in a loss of material. The apparent specific gravity of a porous carrier is not a direct index to its value in thus increasing the catalyst exposure, because, as in the case of pumice, some of the pores are closed bubbles with no outlet to the surface. It is only pores which extend to the surface that are effective in this sense. It should not be overlooked, however, that the evaluation of this increased surface effect is almost impossible and that its efficiency must vary with the reaction occurring.

Aside from this effect, porous carriers have an advantage in their ability to hold the catalyst firmly in place. Solid catalyst carriers, such as granular metal, should simulate the porous carriers in having a rough surface to which the active catalyst material may be firmly bonded. This is especially important in the case of reactions which are conducted at high space velocities where the tendency is to blow the catalyst from the support and out of the reaction chamber.

When a choice of catalyst size and shape may be made as in the case of molded supports, consideration should be given to the effect of granule configuration on the free space for passage of the reacting gases relative to the amount of surface exposed. The use of small particles or mixed sizes results in high resistance to the passage of reacting materials, a practice to be avoided because of the cost of compression of reactant gases and vapors. In practice, catalyst supports molded in spherical, cylindrical, and tubular shapes have been used. Each form of support fulfills a special purpose and the forms are generally not directly interchangeable.

Time of contact, or time of exposure of reactants to catalyst and temperature, is determined by calculation from such data as pressure, gross voids between the granules of the catalyst mass, volume of gases undergoing reaction per unit of time, and temperature. The time of contact is an important factor in the study of catalytic, gas phase reactions, and the lack of details and standardized nomenclature in the literature often make it difficult to interpret results in a logical way. The pressure is easily measured, the gross voids in the catalyst mass determined by displacement of a liquid, the amount of material undergoing reaction measured by use of meters or orifices, and the temperature averaged from measurements made over the catalyst mass. Negligence in reporting on these factors has detracted from the value of much experimental work.

Various theories have been advanced to explain the mechanism of catalysis, some of which may be considered briefly. In general, they may be classified as being based on (a) purely physical, (b) physical-chemical, and (c) more or less purely chemical conceptions.

Explanations which may be regarded as belonging to the first class have been chiefly concerned with the part played by adsorption (and, therefore, by surface) in catalytic processes. The fact, for example, that metals such as platinum and palladium which act as catalysts in hydrogenation and

dehydrogenation reactions, are known to possess the property of adsorbing hydrogen in large quantities, led to the view that the function of the metal as a catalyst depended in some way upon its purely physical properties. That some such relationship exists would seem to be substantiated, moreover, by the observation that variations in the condition of the surface of a given adsorbent, due to differences in its method of preparation, produce marked changes both in its adsorptive power and in its catalytic activity. Thus, for example, platinum black takes up considerably larger quantities of hydrogen than does platinum sponge and is at the same time a much more active catalyst in reactions involving hydrogen.

Adsorption in such cases is regarded simply as an accumulation of the gas at the surface of the metal and the increase in catalytic activity is assumed to be due to an increase in the velocity of the reaction arising from an increase in the concentration of one of the components of the reacting system. If this assumption is true it follows, however, that catalytic activity should vary directly with adsorptive power. Catalysis would then be as Ostwald [38] defined it, only the acceleration of a chemical phenomenon which otherwise would take place slowly. This aspect of the problem has been made the subject of exhaustive investigation and an effort made to prove or disprove certain deductions which depend upon the veracity of the theory: viz.,

(1) Those gases which are most readily liquefied should be adsorbed to the greatest extent by a given catalyst. This relationship has been studied in its various aspects by Benton [33] Lamb, Bray and Frazer,[34] Taylor and Burns,[35] Langmuir [36] Mond, Ramsay and Shields [37] and others. Their results would seem to indicate that while in certain cases a striking parallelism exists, it is not possible to demonstrate any definite relationship between any two sets of properties.

(2) An adsorbent should not show specific adsorption for different gases. Here the exact opposite has been noted so frequently that preferential adsorption would seem to represent the rule rather than the exception. It has been shown,[39] however, that the relative amounts of oxygen, nitrogen, hydrogen, carbon monoxide, carbon dioxide, and argon adsorbed on glass or mica were in the same order as the boiling points of the gases, showing that the forces involved were secondary valence forces such as those involved in liquefaction. In the case of platinum, however, the phenomena were such as to indicate that the gases were held by primary valence forces at high temperatures and by secondary valence forces at liquid air temperatures. The layer adsorbed on the solid was never more than one molecule or atom deep.

(3) The affinity of the adsorbent for the adsorbed substance would

[33] Benton, *J. Am. Chem. Soc.* **45**, 887 (1923).
[34] Lamb, Bray and Frazer, *J. Ind. Eng. Chem.* **12**, 213 (1920).
[35] Taylor and Burns, *J. Am. Chem. Soc.* **43**, 1273 (1921).
[36] Langmuir, *J. Am. Chem. Soc.* **40**, 1361 (1918).
[37] Mond, Ramsay and Shields, *Z. physik. Chem.* **25**, 657 (1896).
[38] Ostwald, *Rev. Sci.* 1902, (1), 640.
[39] *J. Am. Chem. Soc.* **39**, 1904-5 (1917).

be of the nature of mass for mass and so would be unaffected by the presence of minute quantities of foreign substances. It follows, moreover, that the reacting film should be of unlimited thickness. Neither deduction is in accord with the actual facts of experiment.[40] Other deductions following from this purely physical conception of catalysis are equally untenable and it would, therefore, seem reasonable to conclude that the mechanism of catalysis cannot be fully accounted for on the basis of purely physical conceptions.

Without wholly discarding these conceptions a second group of theorists seek to explain the phenomena on what may be called a physical-chemical basis. In doing so they emphasize the importance of surface action. They differ from those holding to the purely physical conception by supposing that the surface attraction of the catalyst for one or more components of the reacting system is not merely that of mass for mass, but that some form of loose chemical reaction is involved. In this way they attempt to account for the observed phenomena of specific adsorption, while at the same time discarding the idea that intermediate compounds of definite composition are formed during the course of any given catalytic reaction. Adsorption by the catalyst of one or more components of the reacting system is understood in general to imply the formation of a unimolecular layer of one of the reactants on the surface of the catalyst and is assumed to be due to the existence on this surface of unsaturated fields of force.

That surface, even in the case of what may be termed catalytically inactive substances, has an important influence upon the velocity of chemical reactions has been repeatedly demonstrated. For example, the introduction of glass wool has been found to increase the rate of reactions taking place in glass vessels in proportion to the increase in surface. In studying this action of various surfaces it has been found that the condition of the surface plays a prominent part in determining the velocity of chemical reactions. Beyond the visible unevennesses of surfaces (where catalytic influences might be explained as resulting from an increase in concentration due to capillary absorption) the manner in which a given surface has been laid down would seem to be of the utmost importance. Thus, for example, electrolytic copper is not effective as a catalyst in the dehydrogenation of alcohol, whereas copper prepared in other ways may be extremely active.[41]

Differences in the catalytic activity of one and the same metal under different conditions of physical aggregation is generally conceded by theorists of this school to be due to differences in the number and degree of unsaturation of surface fields of force. This view is supported by certain lines of experimental evidence. For example, an X-ray study of crystal structure has shown that the atoms are evenly spaced. Thus, the

[40] *Compare* a. Von Hemptinne, *J. Phys. Chem.* **27,** 42 Soc. **38,** 2268 (1916); c. Lowry and Hulett, *J. Am. Chem* [41] a. Hinshelwood, *J. Chem. Soc.* **123,** 2725 (1923); 12 *Soc.* **110A,** 298 (1926); *also compare* c. Gauger, *J. Am. Cl*

molecule is probably not the unit of the crystal but the crystal itself is a unit in the interior of which each atom has its affinity neutralized in all directions by its neighboring atoms. Under these conditions it is obvious that an atom on the surface would be partially unsaturated. Langmuir [42] has developed these and similar ideas in great detail.

The corollary to this hypothesis is that a layer of atoms not exceeding unity in thickness would be attracted and held by such a layer of unsaturated surface atoms. Experimental evidence in support of this deduction has been furnished as a result of investigations by Gauger and Taylor [43] and by Constable [44] upon the effect of pressure on adsorption. That the whole surface of the catalyst is not uniformly active would seem to be established from consideration of the following facts: (1) The quantity of poison which is sufficient to reduce catalytic activity to zero is frequently so minute, that it would not possibly cover more than a very small fraction of the total surface of the catalyst.[45] (2) The saturation capacity of nickel for hydrogen varies with the temperature, thus indicating that the number of spaces which can be occupied by gas molecules is less at high temperatures than at low.[46]

Assuming then that surface phenomena play an important rôle in catalysis and that unsaturated centers or fields of force exist on these surfaces, it follows that the mechanism of catalysis depends primarily upon the precise way in which these function. According to Taylor [47] the distribution of such centers is pictured in terms of peaks and valleys. Just as an atom on the surface of the catalyst might be assumed to possess a greater degree of unsaturation than an atom in the interior, so a peak atom might be regarded as being still more unsaturated. Variations in the degree of unsaturation might thus be assumed to determine the potentiality of activity of different active centers, peak atoms having the highest potential. Palmer and Constable,[48] on the other hand, are inclined to think that the key to the situation lies in the orientation of the surface atoms and attempt in this way to account for differences in activation which result from differences in the method of preparation of a given catalyst. Their views are based upon the fact that they have been able to demonstrate the existence of a definite orientation in their film of metal and that certain planes have been found to be more effective than others in catalytic reactions. Still another theory attempts to explain differences in degree of activation as due to differences in the size of atomic or molecular pores, or, in other words, as due to differences in the actual distances which exist between active centers. This theory is supported by a large body of experi-

[42] Langmuir, *J. Am. Chem. Soc.* **38**, 2221 (1916).
[43] Gauger and Taylor, *ibid.* **45**, 920 (1923).
[44] Constable, *Proc. Roy. Soc.* **107A**, 279 (1924).
[45] Armstrong and Hilditch, *Trans. Faraday Soc.* **17**, 670 (1922).
[46] Gauger and Taylor, *loc. cit; also compare* Pease, *J. Am. Chem. Soc.* **45**, 1195 and 2235 (1923).
[47] *Proc. Roy. Soc.* **108A**, 105 (1925).
[48] a. Palmer, *Proc. Roy. Soc.* **98A**, 13 (1920); **99A**, 412 (1921); **101A**, 175 (1922); b. Constable, *ibid.* **108A**, 355 (1925); **110A**, 283 (926); c. Constable and Palmer, *ibid.* **106A**, 250 (1924); **107A**, 255, 270, 279 (1925).

mental evidence.   For example, Adkins [49] in studying the catalytic effect of alumina prepared in different ways upon the reaction—

$$HCOOH = CO + H_2O$$
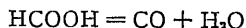
has been able to demonstrate that the velocity of the decomposition varies with the actual size of the pores, being greatest in the case of colloidal alumina (crystal units of the order of 4^{-7} cm.) and least in the case of alumina prepared from the isopropoxide (crystal units of the order 8^{-0} cm.)

Methanol catalysts composed of zinc and copper oxides are decidedly crystalline in structure as evidenced by an X-ray examination.   Although catalysis is ordinarily thought to be a surface effect, it seems to be closely
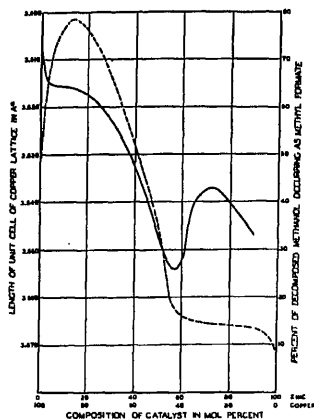
FIG. 2.—Expansion of copper lattice compared with methyl formate production (dotted), both as functions of catalyst composition in the decomposition of methanol over Zn-Cu catalysts. [50]
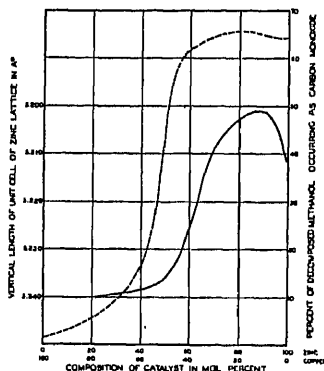
FIG. 3.—Change in zinc oxide lattice compared with carbon monoxide formation (dotted), both as functions of catalyst composition in the decomposition of methanol over Zn-Cu catalysts. [50]

associated with the internal crystalline structure of the catalyst, as has been shown by Frolich and his associates. [50] By varying the composition of the zinc-copper catalyst it was found that the crystal lattice of both catalyst components changed with composition. The nature of the products from the decomposition of methanol over these catalysts at atmospheric pressure was found to undergo changes quite markedly in accord with the changes in crystal structure of the catalysts.   The similarity of the curves shown in Figures 2 and 3 is such as to preclude the assumption that it may be merely coincidental.   Although the mechanism of the decomposition is profoundly influenced by the catalyst composition, the total decomposition

[49] Adkins, *J. Am. Chem. Soc.* **44**, 385 (1922); **45**, 809 (1923); **46**, 130 (1924).
[50] Frolich, Davidson and Fenske, *Ind. Eng. Chem.* **21**, 109 (1929).

is only slightly affected, showing that the principal effect of catalyst composition is to determine the selectivity in directing the reaction. An explanation for this singular relationship has not been advanced, but may be involved in the changes induced in the residual forces as valences of the surface atoms by the changing interatomic distances.

In the preceding discussion it will be noted that while the idea f chemical attraction has been introduced in order to account for the selective action of the catalyst, no attempt has been made to define the chemical character of any of the combinations which are assumed to result from union of the catalyst and the reacting particles. Indeed such combinations are specifically assumed to be of a physical-chemical rather than of a purely chemical nature and the resulting compounds would, therefore, of necessity be of a more or less indefinite and indeterminate character.

Another school of thought attempts to define the nature of such addition products somewhat more exactly by supposing that they represent perfectly definite though very unstable chemical compounds which result from the interaction of the catalyst with one or more of the components of the reacting system and which later decompose with the liberation of the catalyst and the formation of the end products of the reaction. This theory, based as it is upon the assumption of the formation of *intermediate compounds,* is primarily concerned in defining and demonstrating the actual existence of such substances.

A consideration of the following facts will show that in the course of the study of the mechanism of catalysis considerable support has from time to time been given to this theory. Rice and Marcet as early as 1828 postulated the formation of an oxide of platinum in order to account for its behavior in certain catalytic reactions.[51] The preparation of ether from alcohol by the action of sulfuric acid is a well-known reaction which is commonly interpreted as due to the formation and subsequent decomposition of an intermediate compound, namely $C_2H_5 \cdot HSO_4$, and in this case the supposed intermediate has actually been isolated. In studying the catalytic decomposition of potassium chlorate in the presence of manganese sulfate, Dhar[52] was able to detect the presence of potassium permanganate. Since the latter is known to decompose at $250°$ C. while potassium chlorate decomposes at $450°$ C., the conclusion was reached that catalytic decomposition was due to the formation of potassium permanganate as an intermediate compound.

Langmuir has postulated that the only difference that exists between tungsten oxide and the adsorption complex formed between oxygen and tungsten is that in the case of the oxide the linkages between tungsten atoms are completely obliterated whereas in the case of the adsorption complex the tungsten atoms remain linked together. When nickel acts as a hydrogenation catalyst the nickel-hydrogen complex differs from

[51] *See* Engler and Wöhler, *Z. anorg. Chem.* **29**, 1-21 (1902).
[52] Dhar, *J. Phys. Chem.* **28**, 948 (1924).

nickel hydrides only in that the hydrogen is not sufficiently powerful to pull the nickel atoms from each other in the case of the complex. Carbon monoxide, however, is sufficiently powerful to pull nickel or iron atoms from each other and form gaseous metallic carbonyls of definite composition. The physical view of adsorption as influenced by chemical forces ... primary or secondary valences is considered to be identical with the chemical hypothesis of unstable intermediate compound formation in hydrogenation reactions over metallic catalysts.[53] The primary reaction is the formation of a compound between the catalyst and one of the reactants; this compound then reacts further with the other reactant to give the final product which separates from the catalytic surface to allow the cycle to be repeated.

Even when the actual compound itself cannot be isolated, the formation of intermediate products during the course of catalytic reactions would seem to be indicated from a study of color and other changes in the catalytic mass. Thus, for example, in the decomposition of hydrogen peroxide in the presence of mercury, there is visible evidence of the formation of a film which later breaks down. In oxidations of gaseous hydrocarbons in the presence of vanadium oxide, definite changes in the color of the catalyst from blue-green to orange have been observed. Since these have been found to accompany changes in the relative percentages of the oxides of vanadium (V_2O_3, V_2O_4, and V_2O_5) present in the catalytic mass at different temperatures, the phenomenon has been associated with alternate oxidations and reductions of vanadium, but is probably much more complicated.[54] Again, in the oxidation of ammonia to nitric acid in the presence of manganese dioxide, a definite color change from black to a light yellowish brown takes place. If, however, a promoter such as silver oxide or copper oxide is used, very little reduction is observed and this is explained by assuming that in the process of alternate oxidation and reduction, oxygen is continuously supplied to the manganese by means of the promoter.[55] Still another illustration is to be found in the familiar phenomenon of the oxidation of mixtures of methyl alcohol and air to formaldehyde by means of copper. In this case, the color changes are most readily interpreted by assuming alternate oxidation of the copper to copper oxide and reduction to the metal or a lower oxide.[56] The extreme of a chemical viewpoint on this subject is expressed by Ipatiew[57] who goes so far as to state that only those metals which are readily oxidized and reduced can serve as effective catalysts in the oxidation of the alcohols.

That the same phenomenon is susceptible of more than one interpretation is, however, shown by the fact that Sabatier and Senderens[58] offer a very plausible explanation of the oxidation of the aliphatic alcohols by

[53] Armstrong and Hilditch, a series of papers on "Catalytic Actions at Solid Surfaces" published in *Proc. Roy. Soc. (London)*, 1919 to 1921.
[54] Weiss, Down and Burns, *J. Ind. Eng. Chem.* 15, 965 (1923).
[55] Piggot, *J. Am. Chem. Soc.* 43, 2034 (1921).
[56] Cf. Pease and Taylor, *J. Am. Chem. Soc.* 43, 2279 (1921); 44, 1637 (1922).
[57] *Ber.* 34, 594, 3576 (1901).
[58] *Compt. rend.* 134, 691 (1902).

assuming that the process is one of dehydrogenation and that the metal functions in the formation of an unstable hydride. This view has obtained a considerable amount of support from study of certain metallic hydrides.[59]

Some quantitative calculations in regard to intermediate compound formation have been possible in the synthesis of ammonia over active iron catalysts. Almquist [26] has calculated that the difference in free energy between crystalline iron and the more active iron atoms is of the order of 12,000 calories per gram atom of iron. In supporting the theory of intermediate nitride formation, Emmett and Brunauer [60] compared their own results with the calculations of Frankenburger,[61] who showed that an excess free energy of 12,000 calories or more per gram atom for the active iron would permit the formation of Fe_2N on the active atoms by a pressure of three or four atmospheres of nitrogen at 377° C. The new calculations show that at 444° C. a pressure of 100 atmospheres of nitrogen is necessary to form Fe_4N at the active points, a result that makes the reduction of surface Fe_4N by hydrogen to form ammonia seem an entirely feasible mechanism for the synthesis.

Even when there seems to be no direct evidence for the formation of intermediate compounds in catalytic reactions, sufficient indirect evidence frequently exists to make this a plausible hypothesis. For example, a study of the absorption curves of several unsaturated oils have led Armstrong and Hilditch [62] to assume the formation of an intermediate compound between the catalyst and the organic residue in certain types of reactions. The catalytic action of iron in the formation of methane from carbon monoxide and hydrogen has been accounted for by assuming the formation of iron carbonyl.[63] The action of nickel, functioning in the same reaction, has been interpreted similarly.[64] Another explanation of the synthesis of methane depends, however, upon the assumption that the intermediate formation of formates of the different metals which may be used as catalysts plays an important part in this reaction.[65] This mechanism is particularly interesting because of the fact that it can be used to account for a number of different catalytic processes.[66] Analogous to such cyclic formations and decompositions of formates is the process by which acetone is now manufactured. The earlier procedure involved the preparation of calcium or barium acetate and its subsequent decomposition under the action of heat. Both processes may now be made to take place simultaneously by passing the vapors of acetic acid through heated iron tubes containing barium hydroxide.

[59] Mond, Ramsay and Shields, *Chem. News* **76**, 317 (1897).
[60] *J. Am. Chem. Soc.* **52**, 2682-93 (1930).
[61] a. *Z. Elektrochem.* **34**, 632 (1928); *also* b. Ullmann, "Enzyklopädie der Technischen chemie," Berlin, 1928, Vol. I., p. 393.
[62] *Proc. Roy. Soc.* **96A**, 137, 322 (1919); **97A**, 259 (1920); **98A**, 27 (1920); **108A**, 111 (1925).
[63] Fischer and Tropsch, *Brennstoff Chem.* **2**, 193 (1923).
[64] Medsforth, *J. Chem. Soc.* **123**, 1453 (1925). *Also compare* Mond, *Chem. News* **62**, 97 (1890); Mond, Hirtz and Cowap, *J. Chem. Soc.* **97**, 798 (1910); Mond and Wallis, *ibid.* **121**, 29-32 (1922).
[65] Vignon, *Am. Chem. Phys.* (9) **15**, 42 (1921).
[66] Hofmann and Schibsted, *Ber.* **51**, 1389, 1398 (1918); Brit. Pat. 173,097 (1920) Badische Anilin u. Soda Fabrik.

In explaining the action of free metals as contact catalysts in auto-oxidative phenomena, Moureu and Dufraisse [18] suppose that the catalyst auto-oxidizes to give an unstable oxide, which then decomposes to give up the oxygen and regenerates the metal. Other catalysts probably behave in the same way. Thus, a number of organic substances are oxidized in the presence of active charcoal at ordinary temperatures, and carbon monoxide is oxidized completely at room temperature by the catalytic action of a mixture of metallic oxides known as "hopcalite."

In summary it may be said that while a variety of different mechanisms may be employed to interpret the same phenomenon and while no single hypothesis would seem in any case to be entirely satisfactory to all investigators, it at least seems certain that both physical and chemical factors must be taken into account in seeking for a final explanation of catalytic phenomena. From an experimental viewpoint, however, the theory based on the formation of temporary unstable intermediate compounds between the catalyst and one of the reactants, is useful because of the possibility of foreseeing reactions. This idea furnished a valuable guide to Sabatier in his numerous and extensive investigations on catalysis.[67] For further speculations—representing it is true a wide divergence of opinion—on this subject the reader is referred to such classical treatises as have been published from time to time by Ostwald,[68] Van't Hoff,[69] Mellor,[70] Rideal and Taylor,[71] Engler and Weissberg [72] and others.[73]

The essential object of the present volume is the assemblage and critical review of facts. It has seemed wise, therefore, to espouse no creed and to venture upon no generalizations as to the causes of catalysis, the more especially since so far there has been no one explanation which fits all of the known facts. Indeed, it even appears at present as if the phenomena observed in different cases were the result of different causal agents. This being the case, true progress in this field can be obtained only through a persistent effort to accumulate definite and proven facts until the data are sufficiently extended and complete to justify broad generalizations along tenable lines.

It should be noted that particularly in the case of operations on the commercial scale many other facts besides the nature and physical form of the catalyst itself must be taken into consideration. For example, the progressive loss in activity of a given catalyst, if too rapid, may act as a very serious obstacle to the ultimate success of a commercial process. This is sometimes due to impurities in the reacting substance,—a so-called

[67] Sabatier, *Ber.* **44**, 2001 (1911).
[68] Ostwald, "Uber Catalyse, Vers. Ges. Deutsch Naturforscher und Artze," Hamburg, 1901.
[69] Van't Hoff, "Lectures on Theoretical Physical Chemistry" (Translated), 1899.
[70] Mellor, "Chemical Statics and Dynamics," London, Longmans, Green & Co., 1904.
[71] Rideal and Taylor, "Catalysis in Theory and Practice," New York, Macmillan Co., 1919.
[72] Engler and Weissberg, "Kritische Studien uber die Vorgange Autoxydation," Braunschweig, 1904.
[73] *Consult also* a. Bancroft and Taylor, Reports of the Committee on Contact Catalysis, *J. Ind. Eng. Chem.* **14**, 326, 444, 545 and 642 (1922); *J. Phys. Chem.* **27**, 801-941 (1923); *ibid.* **28**, 897-942 (1924); b. Taylor, *Proc. Roy. Soc.* **113A**, 77-86 (1926), A Review; c. Frankenburger, *Z. angew. Chem.* **41**, 523-31, 561-7 (1928). Bibliography.

poison,—such as for example, arsenic in the sulfuric acid contact process or sulfur compounds in certain hydrogenations. Sometimes this deterioration has been found to be due to a chemical combination between the catalyst and the supposedly inert material used as the support. In purely academic investigations the length of runs is usually too short for the determination of the factors affecting catalyst deterioration and these problems must be solved in commercially feasible processes which should operate for twenty-four hours per day for months at a stretch without catalyst replenishment. The thermal input and output of the reaction when undertaken on a large scale also present problems which are far more vital in the plant than in the laboratory. This phase of the subject, particularly as applied to exothermal reactions, will be dealt with in greater detail in a later chapter. Other factors demanding consideration are the influence of materials used in the construction of the reaction chamber, the mechanical effects in gas mixing, etc. One very important factor is the physical or mechanical stability of the catalyst. With high gas velocities any loss of catalyst due to dusting from the surface of the carrier gradually results in decreased productivity. At high temperatures the vapor pressure of the catalyst itself may be of great importance. Also, the possibility that impurities in the reacting substances may react with the catalyst to form volatile substances must be considered. Thus, in the manufacture of contact sulfuric acid with vanadium catalysts loss of catalyst by volatilization may be due to the use of smelter gases containing fluorine. The change in form of platinum during the oxidation of ammonia with the possibility of loss of catalytic material is an important subject of study. The possible increase in resistance to the flow of large volumes of gases and the blanketing of the catalytic surfaces by inert dust introduced in the gases affect the productivity of the catalyst. These and a multitude of other mechanical details must by their very nature be considered in their relation to specific reactions and will, therefore, be reserved for discussion later in this volume. It must not be forgotten, however, in any resumé of the theories of catalysis that these and similar factors present serious problems in the actual carrying through of any catalytic plant project.

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Chapter II

Catalytic Decomposition of Alcohols

Numerous difficulties are presented by catalytic processes which involve the oxidation of even simple organic compounds. In the case of such substances, the problem is complicated not only by the fact that a large number of parallel reactions which involve different types of oxidation are possible, but also by the fact that all organic molecules tend to undergo complex dissociations and polymerizations at elevated temperatures. The polymerization and condensation products may in turn be oxidized, either partially or completely. As a result, the final products of the oxidation of even relatively simple organic compounds may result in the formation of very complex mixtures, difficult to separate and practically useless from an economic standpoint. In order to obtain pure substances in good yield, as the result of any given oxidation it is necessary to study the reaction experimentally under the greatest possible variety of conditions.

As an aid to a better understanding of some of the difficulties presented by the catalytic oxidation of organic compounds in the vapor phase, particularly from the chemical reaction standpoint, the problems involved in the oxidation of alcohols and the means used to overcome them have been chosen for discussion first.

In the case of any given organic compound the study of oxidation processes is best preceded by a preliminary investigation of its behavior under the action of elevated temperatures alone and in the presence of catalytic materials. Since ethanol has been studied in greater detail than any other alcohol and affords an exceptionally good illustration of the behavior of primary alcohols when subjected to catalytic oxidation in the vapor phase, the chemistry of this particular substance will be discussed first. The actions of alcohols higher than ethyl will be discussed, whereever data are available, in general, as they are related to the actions of ethyl. Because it occupies a unique position by virtue of being the lowest member of the aliphatic alcohol series, methanol will be discussed as a separate subject.

The decompositions which alcohols undergo at the temperatures used in oxidation processes and in the presence of active oxidation catalysts are of sufficient importance and have been studied in such detail that special consideration is necessary. It is the purpose of this chapter to point out these pyrolytic and catalytic reactions from a chemistry standpoint. No at-

tempt has been made to indicate industrial methods of the applications of such decompositions except as they are incidental to the discussion.

Decomposition Reactions of Ethanol

When ethanol is subjected to elevated temperatures it tends to undergo one or more of the following *major* transformations:

$$\text{I.} \quad C_2H_5OH = CH_3CHO + H_2$$
$$\text{II.} \quad C_2H_5OH = CH_2{=}CH_2 + H_2O$$
$$\text{III.} \quad 2C_2H_5OH = (C_2H_5)_2O + H_2O.$$

Under certain conditions, such as exposure to particular catalytic materials, each of these reactions may give yields as high as 50 per cent or more of theoretical. Each of these reactions are reversible, practically completely so, under certain conditions where side reactions and decompositions are largely eliminated. Secondary decomposition of acetaldehyde to methane and carbon monoxide, reduction of the ethylene by hydrogen to ethane, break down of ether to lower molecular weight compounds, polymerizations, etc., so involve any equilibrium relations that the relative rates of the different reactions as well as the equilibria are difficult to obtain experimentally. Even where specific and directive catalysts are used, side reactions are present and complicate any precise analysis of the decomposition mechanism.

The three major reactions shown above belong to two general classes or types of chemical transformations: (1) dehydrogenation and (2) dehydration processes. These two types are usually associated with specific catalysts which favor one process to the more or less exclusion of the other. Consideration of the two types of reaction, particularly in regard to the catalytic activity of various materials in furthering them and in inducing or suppressing side reactions will serve to show the limitations that must be placed on the oxidation process to prevent loss of material or complication of recovery.

When the reactions are brought about by elevated temperatures and in the absence of oxygen or other oxidizing gases, the actual method usually consists in passing the substance in the form of vapor through heated tubes, the walls of which may or may not act as catalysts toward the reaction. In the case where no catalytic action occurs, the initial temperature for reaction must be higher than when catalysts are present. Thus,[1] ethanol when passed through a hard glass tube at 700° C. shows only slight decomposition and simply distils over through the tube without appreciable loss in weight. At 800° C. decomposition becomes noticeable and is accompanied by the formation of gases and traces of acetaldehyde. At 820° to 850° C. decomposition becomes energetic. The temperature at which the reaction is made to occur is not the only factor affecting the non-catalytic decomposition. It is evident that the length of time that

[1] Ipatiew, *Ber.* **34**, 3579 (1901).

the vapors are subjected to the temperature, i.e., the time of contact, is an important factor. Thus, long times of contact at low temperatures may give decompositions of the same magnitude, although not necessarily of the same kind, as short times of contact at high temperatures. Thus, a temperature of 500° C. has been reported as the initial temperature for ethanol decomposition in contrast to the much higher value given by Ipatiew for comparable experimental conditions.[2] It is probable that either differences in time of contact or differences in methods of temperature measurement would account for these discordant results. Under the conditions of the higher temperature experiments the yields of acetaldehyde are low because of the fact that the dehydrogenation of the alcohol is always accompanied (a) by simultaneous dehydration of the alcohol with the formation of ethylene, (b) by decomposition of the aldehyde with the evolution of carbon monoxide and methane and (c) by a variety of other minor reactions the nature of which is not always clearly understood. In cases where ethanol vapors are passed through heated tubes the walls of which are capable of acting catalytically, the initial temperature of the decomposition is very much lower and the decomposition itself is much more complete. The reaction, moreover, proceeds much more definitely in the sense (a) of aldehyde formation (dehydrogenation) or (b) of ethylene or ether formation (dehydration), depending upon the catalytic nature of the material which constitutes the walls of the tube.

Processes of this sort have been classified under the general name of pyrogenic decomposition and may be differentiated into two types: (1) those which take place under the action of heat alone, and (2) those which take place under the action of heat in the presence of a catalyst. In the former case the product of the reaction frequently consists of a very complex mixture, the character of which is determined by the temperature, pressure and time of contact.[3] In the latter case, the course of the reaction may in certain instances be so controlled as to favor the formation of a single product. The procedure may be varied by passing the vapor of the substance through a tube or chamber the walls of which are themselves inactive but into which an appropriate catalyst has been introduced. This latter modification of the reaction has been made the subject of careful investigation by Ipatiew, who was indeed the first to call attention to the definite quantitative differences in the amounts of (a) acetaldehyde and (b) ethylene which resulted from the pyrogenic decomposition of ethanol under the action of specific catalysts.

Dehydrogenation Reactions of Ethanol

As has been stated above,[1] when alcohol vapors are passed through a glass tube at 700° C. very little decomposition occurs. At 800° to 830° C.

[2] Bertholet and Jungfleisch, "Traite elementaire de Chemie organique," 1886, 2nd. Ed., Vol. I., p. 256.

[3] *Compare* the work of Bethelot (*loc. cit.*); Ipatiew, Sabatier, Senderens and E. Peytral, *Bull. soc. chim.* (4) 27, 34 (1920).

about 80 per cent of the alcohol which is decomposed is converted into acetaldehyde and hydrogen while 20 per cent yields ethylene and water. If the tube is made of platinum, active decomposition begins at a lower temperature (780° C.) and a much greater percentage of alcohol is decomposed. Of this, approximately 86 per cent is converted into acetaldehyde and 14 per cent into ethylene. In this case, however, about 90 per cent of the aldehyde which is formed decomposes to methane and carbon monoxide. In the presence of zinc the reaction occurs at an even lower temperature—the zinc remains unchanged and the proportion of aldehyde to ethylene decomposition varies with the physical condition of the metal.[1] When rods of zinc are used in a glass tube at 620° to 650° C., the yield of aldehyde amounts to 80 per cent of the alcohol decomposed and very little ethylene is produced. In this case only a relatively small amount of the aldehyde is lost as a result of secondary decompositions. When zinc dust [4] is employed in a glass tube at 550° C., approximately one-half of the alcohol is converted into acetaldehyde and one-half into ethylene and water. Secondary reactions which involve the decomposition of aldehyde and also of a large part of the water take place under the above conditions. With filings of brass containing 33 per cent of zinc in a glass tube at 660° C., results are obtained which are practically identical with those which have been described in the case of zinc rods. The conclusion drawn by Ipatiew from a comparative study of the action of a large number of metals, i.e., sodium, magnesium, aluminum, manganese, nickel, iron, cadmium, copper, tin, bismuth, antimony, and zinc as catalysts in the decomposition of ethanol was that only those which decompose water readily (i.e., are easily oxidized and reduced) have the power to lower the temperature for alcohol decomposition. The mechanism of the process is explained by Ipatiew on the assumption that ethanol first breaks down to give ethylene and water. The water then reacts with the metal, forming free hydrogen and the metallic oxide (Fe_2O_3, PbO_2, MnO_2, SnO_2, CuO, ZnO, etc.), the latter being immediately reduced by the action of a second molecule of alcohol.

$$C_2H_5OH = C_2H_4 + H_2O$$
$$Me + H_2O = MeO + H_2O$$
$$C_2H_5OH + MeO = CH_3CHO + H_2O + Me$$
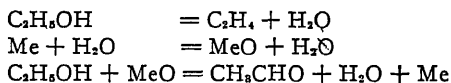
This view of the phenomena led Ipatiew to a study of the behavior of alcohol in the presence of various metal oxides [5a] but as the results of this investigation showed that the oxides of zinc, iron and tin produced effects which were practically identical with those of the corresponding metals, he did not pursue the study further.

This mechanism which Ipatiew proposed was based on his idea that the normal reaction was dehydration and has been consistently refuted by

[4] For the action of zinc dust on alcohol at 300 to 350° C. in a glass tube *compare* Jahn, *Ber.* 13, 987 (1880). At this temperature the product consisted largely of $C_2H_4 + H_2O$ while at red heat CO and CH_4 were obtained.
[5a] Ipatiew, *Ber.* 35, 1047 (1902).

subsequent workers. Sabatier showed that no trace of ethylene or water occurred among the decomposition products over copper catalysts and that the dehydrogenation reaction took place directly. Copper does not reduce water even at 800° C.[5b]

The lower aliphatic alcohols are, in general, easily dehydrogenated to form aldehydes and ketones by passage over reduced copper at temperatures of about 300° C.[6] Copper catalysts do not promote the secondary decomposition of acetaldehyde to methane and carbon monoxide as do several of the other metallic catalysts. Sabatier and Senderens [7] have shown by their experiments that finely divided copper is preëminent among the metals in its ability to facilitate aldehyde formation from alcohols. They claim that in order for the metal to show its fullest efficiency it must be prepared by the reduction of a semi-light oxide at a temperature of about 180° C. and without incandescence. If a heavy oxide is used, the catalyst is apt to be poor and if a too light oxide, it is apt to be so active as to bring about destructive decomposition of the alcohol. Properly reduced copper catalyzes the dehydrogenation reaction at temperatures of from 220° to 300° C. Above 300° C. aldehyde decomposition takes place with formation of methane and carbon monoxide. The homologs of ethanol behave in the same way, although at somewhat higher temperatures. Copper in a solid form does not act as a good catalyst in alcohol decomposition.

Since copper is also readily oxidized and reduced it can easily be made into highly porous and rigid forms.[8] This has been accomplished as follows: Fused cuprous oxide is made by either melting black cuprous oxide or by burning copper turnings in air at a temperature of about 1200° C. The resulting oxide is bluish black and may be granulated to the desired size particles. This oxide is reducible at temperatures as low as 220° to 300° C. and retains its size during reduction so that very porous masses of spongy copper high in catalytic activity may be thus formed. These porous granules are hard and strong physically, very desirable features for a catalyst to have as the use of deep layers is permitted without the possibilities of packing and channeling. With alcohols of low molecular weight, such as ethyl or isopropyl, the copper oxide may be reduced by the alcohol at temperatures of 280° to 300° C. and the use of hydrogen for the reduction dispensed with. For this purpose, the alcohol is merely vaporized from a still, preheated to about 300° C. in a copper coil and passed over the oxide material which is also heated.

$$Cu_2O + C_2H_5OH = 2Cu + H_2O + CH_3CHO$$
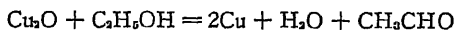
With the higher alcohols, preliminary reductions of the oxide with hydrogen is necessary.

[5b] Maier, *Ind. Eng. Chem.* 22, 916 (1930).
[6] Sabatier and Senderens, *Compt. rend.* 136, 738, 921, 983 (1903).
[7] a. Sabatier and Senderens, *Ann. chim. phys.* (VIII.) 4, 319-431, 433-488 (1905); b. *also,* Sabatier, *Ber.* 44, 1984-2001 (1911).
[8] Brit. Pat. 173,004 (1920) Legg and Adam.

The dehydrogenation of ethanol over copper catalysts is not complete at 300° C. when moderate times of contact are used; but if the temperature is raised to 350° C. or higher, secondary reactions become more and more evident. At temperatures above 350° C., copper catalysts begin to activate the decomposition of acetaldehyde to methane and carbon monoxide, to induce polymerization of the aldehyde, to cause dehydration processes to set in, to cause hydrogenation of the ethylene, and, in general, to promote secondary decompositions and condensations which complicate the product and destroy the activity of the catalyst. Hence, for the production of aldehydes and ketones it is desirable to use moderate temperatures of about 300° C. and to obtain maximum yields from the decomposition rather than maximum decomposition of alcohol per pass over the catalyst.

The presence of water in the ethanol improves the yields of acetaldehyde relative to the hydrogen produced by suppressing decomposition reactions. Armstrong and Hilditch [9] showed that at 300° C. in the presence of copper catalysts anhydrous ethanol gave an aldehyde-hydrogen ratio of 67 per cent, whereas alcohol containing 8 per cent water gave a 95 per cent ratio showing that aldehyde decomposition had been largely suppressed. Very little methane and carbon monoxide are present in the gas when aqueous ethanol is used. Acetaldehyde when passed over the same catalysts at 300° C. decomposes to the extent of only 15 per cent when water is present in excess of the aldehyde. With approximately equal amounts of water and aldehyde present the decomposition is 24 per cent, while with only small amounts of water as much as 50 per cent of the aldehyde may be lost. The experimental data do not, however, give the various times of contact so that a strict interpretation is not possible although the aldehyde decomposition results qualitatively check those obtained in the alcohol decomposition.

Palmer [10] found that although ethanol decomposed to acetaldehyde in the presence of copper at 300° C. without the formation of secondary decomposition, this was not true when aldehyde alone was used. If hydrogen and acetaldehyde are passed over copper at 250° to 300° C. much of the aldehyde decomposes into secondary products. This anomaly, Palmer explains on the basis of the alcohol being selectively adsorbed by the catalyst surface so that the copper surface is covered with a layer of alcohol molecules which prevent the adsorption and consequent destruction of the aldehyde. The three steps in the dehydrogenation reaction were postulated to be: (1) adsorption of alcohol, (2) activation of certain alcohol molecules, (3) evaporation of hydrogen and acetaldehyde from the catalyst surface.

Acetaldehyde decomposes into methane and carbon monoxide when heated in borosilicate glass tubes at 300° to 350° C. [11] In the presence of

[9] Armstrong and Hilditch, *Proc. Roy Soc.* **97A**, 259 (1920). U. S. Pat. 1,764,962 (1930) Lacy, assr. to Van Schaack Bros. Chem. Works.
[10] Palmer, *Proc. Roy. Soc.* **98A**, 469 (1900).
[11] Bone and Stockings, *J. Chem. Soc.* **85**, 724 (1904); **87**, 910 (1905).

porous porcelain and at a temperature of 450° C. the reaction is more complex, polymerization and condensation reactions occurring, followed by the decomposition of the resulting larger molecules. The gas analysis of such a decomposition shows the presence of 58.5 per cent CO_2, 6.7 per cent CO, 31.0 per cent CH_4, 3.1 per cent H_2, 0.7 per cent C_2H_4. Croton aldehyde and other unsaturated aldehydes may form. The porcelain evidently induces aldol condensation and the elimination of a water molecule results in the formation of croton aldehyde. These reactions are slow, however, and relatively long times of contact are required compared with those effective in the presence of active catalysts, such as some of the finely divided metals. The passage of air with acetaldehyde vapors over catalysts having several degrees of oxidation or over heated metals as copper, silver, nickel, platinum, etc., may result in the formation of formaldehyde.[12]

Various copper alloys have been proposed for the purpose of prolonging the life of the catalyst,[13] and methods have been devised for forming active surfaces on copper masses. Copper metal in the form of particles is treated to form a salt on the surface or copper salts are deposited on the surface of such particles. This salt is then precipitated on the metal surface in a readily reducible form such as hydroxides, and reduced *in situ* to form a highly active catalytic surface on the copper particles.[14] The activity of the reduced copper catalysts is promoted by the addition in a finely divided state of difficultly reducible oxides or phosphates.[15] Readily decomposable copper compounds such as copper formate are also used to give porous masses which are very active catalytically.[16]

The work of Constable and Palmer [17] regarding the mechanism of catalyst action when alcohol is decomposed in the presence of copper catalysts, has contributed valuable information from a physical-chemical standpoint on the manner in which catalysts act. In the presence of their catalysts, the rate of dehydrogenation of ethanol, propanol, and butanol was the same notwithstanding that the length of the hydrocarbon chain had doubled in the series of alcohols. With isopropanol the velocity was five times that of the others. All primary alcohols, however, contain the $-CH_2OH$ group at the end of the hydrocarbon chain and to explain the action of these alcohols these workers have undertaken to show that the primary alcohols are adsorbed by the catalyst surface with the $-CH_2OH$ group in contact with the surface and the hydrocarbon chains perpendicular to that surface. Such an orientation would then make all of the alcohols alike as far as the catalyst surface was concerned and, hence, make their

[12] Brit. Pat. 178,842 (1923) Consortium Elek. Ind.
[13] U. S. Pat. 1,555,539 (1925) Williams to Roessler and Hasslacher Chem. Co.
[14] U. S. Pats. 1,375,345 (1921); 1,375,665 (1921) Backhaus, assr. to U. S. Industrial Alcohol Co.
[15] French Pat. 675,076 (1929) I. G. Farbenind.
[16] Brit. Pat. 158,906 (1922); 175,238 (1922); U. S. Pat. 1,410,223 (1922) Badische Anilin u. Soda Fabrik.
[17] Constable and Palmer, *Proc. Roy. Soc.* (a) 98A, 13 (1920); (b) 99A, 412 (1921); (c) 101A, 178 (1922); (d) 106A, 250 (1924); (e) 107A, 255-69 (1925).

rates of decomposition the same since reaction was supposed to occur in an adsorption film covering the catalyst which at 280° C. was one molecule thick.

Reduced nickel is a much more active catalyst than copper toward the dehydrogenation of ethanol. At 250° C. reaction is pronounced, but even at this low temperature nickel is a powerful catalyst for aldehyde decomposition:

$$CH_3CHO = CH_4 + CO.$$
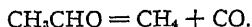
This is shown by the facts that the aldehyde-hydrogen ratio is only 35.7 per cent and the gas composition shows 60 per cent hydrogen, 20 per cent carbon monoxide, and 15-17 per cent methane. The presence of 8 per cent water in the ethanol apparently has no protective effect on the aldehyde as it does in the presence of copper catalysts.[9] Because of this undesirable activity in promoting aldehyde decomposition, nickel catalysts are not applicable to the dehydrogenation of ethanol or alcohols in general.

In common with other catalysts nickel varies greatly in its activity according to the methods that have been used in its preparation. Nickel reduced at 350° to 420° C. is twice as active a dehydrating catalyst toward alcohol as nickel reduced from the same oxide at 300° to 400° C.[18]

The action of nickel is so much more powerful than that of alumina that the dehydrating action of the latter is practically eliminated when catalysts containing mixtures of reduced nickel and alumina are used. In fact, the alumina apparently only acts as a support for the active metal. However, comparative measurements have shown that the oxides of aluminium, iron, magnesium, and calcium may act as strong promoters for nickel catalysts. This effect has been explained as a mechanical effect, viz., the development of a large surface by which relatively more active metal is effectively exposed.[19] When only small amounts of oxide are present the effect is predominantly that of support. The increased addition of oxide may increase the catalytic activity up to a certain point beyond which it only serves to dilute the catalyst and reduce its selectivity. Other explanations of the promoter action postulate the removal of catalyst poisons by the oxide, or regeneration of the active metallic catalyst by oxidations and reductions.[20]

Platinum sponge is even more active than nickel toward the decomposition of both alcohol and aldehyde. Metallic cobalt stands about midway between copper and nickel in activity.

Although acetaldehyde may generally be more economically produced from acetylene by hydration, the high yields that may be obtained by the dehydrogenation of ethanol show the excellent directive powers of the copper catalysts for this reaction. By operating at temperatures below

[18] a. Adkins and Lazier, *J. Am. Chem. Soc.* 46, 2291-2305 (1924); 47, 1719-22 (1920); *see also* b. Rideal, *Proc. Roy. Soc.* 99A, 153, 162 (1921); c. Milligan and Reid, *J. Am. Chem. Soc.* 44, 202 (1922).
[19] Armstrong and Hilditch, *Proc. Roy. Soc.* 103A, 586 (1923).
[20] Schotz, "Synthetic Organic Compounds," New York, D. Van Nostrand Co., 1925, p. 64.

300° C. with such rates of flow that only 25 to 30 per cent of the alcohol reacts per pass yields as high as 90 to 92 per cent of acetaldehyde are obtainable. Continuous operation, however, causes the catalyst to become coated with condensation products which lower the activity. The catalyst activity is restored by oxidation of the organic matter with hot air followed by reduction of the metallic oxide with alcohol. Technically, the aldehyde-alcohol mixture resulting from such a process is separated by fractionation in columns heated with steam. The aldehyde is distilled from the alcohol and condensed. The permanent gases such as hydrogen, with traces of carbon monoxide and dioxide pass out with the aldehyde through the condenser and to a water scrubber where the remainder of the aldehyde is recovered. The alcohol is returned to the dehydrogenating system. Such a process is quite readily made continuous.

Under such conditions the exit gas mixtures may consist of undecomposed alcohol, aldehydes or ketones, hydrogen, and small amounts of carbon oxides and hydrocarbons. This mixture is fractionated in columns built in two sections the lower of which delivers unreacted alcohol, and the upper gives the final alcohol stripping and delivers the aldehyde. The non-condensible gases pass to a scrubber for final recovery of aldehyde or ketone.

Industrially, the dehydrogenation of alcohols to aldehydes and ketones in the presence of metal catalysts is conducted in some instances in apparatus similar in principle and construction to a water tube boiler with inclined tubes. In this case, however, the tubes contain the catalyst and vapors of aldehyde and hydrogen are removed in place of steam.[21] The catalyst may be so distributed in the tubes and the rate of alcohol feed so regulated that the proper time of contact of alcohol vapors is maintained at the correct operating temperature.[22]

Dehydration Reactions of Ethanol

The majority of the metallic oxide catalysts behave with respect to primary alcohols as mixed catalysts, with simultaneous dehydration and dehydrogenation actions. For some of them such as thorium oxide, aluminum oxide, the blue oxide of tungsten, chromium oxide, and silica the dehydrating capacity is predominating. In another group comprising titanium oxide, beryllium oxide, zirconium oxide, uranium oxide, blue molybdenum oxide, ferric oxide the two properties are more nearly equal. A third group containing vanadium pentoxide, zinc oxide, manganese oxides, tin oxide, cadmium oxide, and magnesium oxide the dehydrogenating capacity predominates.[23]

[21] U. S. Pat. 1,454,609 (1923) Winter, assr. to U. S. Industrial Alcohol Co.; *see also* U. S. Pat. 1,437,483 (1922) Backhaus, assr. to U. S. Industrial Alcohol Co.
[22] a. Beauveault, *Bull. soc. chim.* (4) 3, 50, 119 (1908). b. Weismann and Garrard, *J. Chem. Soc.* 117, 328 (1920). c. U. S. Pats. 1,396,389; 1,396,718 (1921) U. S. Industrial Alcohol Co. means for electrically heating catalysts. d. U. S. Pat. 1,396,358 (1921) Cochrane, assr. to U. S. Industrial Alcohol Co., Catalytic apparatus. e. U. S. Pat. 1,388,841 (1921) Backhaus and Arentz, assr. to U. S. Industrial Alcohol Co., description of apparatus and means for purification.
[23] *Compare* Sabatier and Mailhe, *Ann. chim. phys.* (8) 20, 341 (1910).

In investigating the action of carbon as a catalyst, Ipatiew employed a form of graphite mixed with clay which was in general use at the time for the manufacture of crucibles and other forms of laboratory apparatus. This substance, heated in a glass tube at 500° to 600° C., catalyzed the decomposition of alcohol almost completely according to the equation:

$$C_2H_5OH = C_2H_4 + H_2O.$$
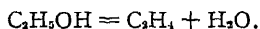
It afforded, therefore, a new method for the preparation of practically pure ethylene.[24] In studying this reaction further, Ipatiew found that the silica present in the clay was not a good catalyst for alcohol decomposition at 600° C. but that alumina in a copper tube had the power to decompose alcohol vapor almost completely at temperatures as low as 380° C. to give ethylene in yields of about 97 per cent.[25] The discovery had previously been made by Grigorief that ethyl and isobutyl alcohols are decomposed by alumina to give olefinic hydrocarbons almost exclusively and that ethers undergo the same decomposition.[26] It remained, however, for Ipatiew to show that the reaction was a general one which was applicable to all alcohols and to establish it upon a quantitative basis.

Following the study of the effect of temperature and pressure upon the catalysis of ethyl alcohol to acetaldehyde or, in general, of dehydrogenation phenomena, Ipatiew extended his investigations into the field of dehydration phenomena using similar apparatus and employing similar methods but varying the type of the catalyst in such a way as to promote the desired reaction. And since previous experimentation had convinced him that practically pure ethylene could be prepared by decomposing alcohol at ordinary temperatures in the presence of alumina he selected clay or kaolin as providing a suitable contact-mass for use in this further investigation. In this connection it may be stated at once that the efficiency of the catalyst was found to vary greatly according to its method of preparation. It is especially important to avoid too high a temperature during the process of calcining since clay so treated was observed to lose its power to dissolve in alkali and in sulphuric acid and also its efficiency as a catalyst. Operating under pressure in iron tubes he found that, in the presence of clay, active decomposition of the alcohol began at 400° C. as compared with 300° C. at ordinary pressures, while in copper tubes the corresponding temperatures are also respectively somewhat higher. In general, it may be said that ethanol decomposition under pressure in the presence of alumina was found to suppress the formation of ethylene with the surprising result that the product of the reaction consisted almost exclusively of ethyl ether:

$$2C_2H_5OH \rightleftharpoons (C_2H_5)_2O + H_2O.$$

[24] Ipatiew, *Ber.* **35**, 1057 (1902). *Compare* Lott and Christiansen, *J. Am. Pharm. Assn.* **19**, 570-1 (1930).
[25] Ipatiew, *Ber.* **36**, 1990 (1903).
[26] Grigorief, *J. Russ. Phys. Soc.* **33**, 173 (1901).

As represented above, this reaction is reversible. Evidence in support of this is found in the fact that the pressure in the apparatus quickly becomes constant, indicating the existence of a condition of equilibrium.[27]

At 450° C. ether begins to decompose to give ethylene and from this point on up to 530° C. alcohol, ether, water and ethylene are all four present as an equilibrium mixture which varies in its percentage composition with the temperature. At 530° C. the pressure of the gaseous system reached a maximum and at this point the ether content of the mixture was equal to 30 per cent. At still higher temperatures the decomposition of the alcohol followed the same general course as has been described as taking place in an iron tube under ordinary pressures. At 620° C., for example, decomposition was accompanied by the formation of carbon, water and a mixture of condensation products.

If ether was substituted for alcohol the same equilibrium mixtures were obtained at all temperatures up to 450° C., which have been mentioned above, provided, of course, that other conditions are identical. This appears to substantiate Ipatiew's opinion that a condition of equilibrium is maintained in the system. Above 450° C. ether decomposes energetically to give ethylene, this latter reaction being in all probability nonreversible. The statement is made, however, that the addition of water vapor to ether seems to hinder decomposition of the ether since no ethylene is formed under these conditions even at temperatures well above 450° C. It is interesting to note that at higher temperatures diolefins were detected among the products of the decomposition of ether. Heated in the presence of an iron catalyst at 570° C. under pressure, ether decomposed to give acetaldehyde as the main product of the reaction.

The use of long times of contact and pressure in ethanol decomposition results in the formation of complex mixtures. Thus, ethanol heated to 425° C. for two hours under high pressure gave a gaseous mixture containing 10.2 per cent carbon dioxide, 31.8 per cent methane, 8.0 per cent ethylene, 7.6 per cent carbon monoxide, 36.6 per cent ethane and the rest hydrogen.[28]

The activity of alumina as a catalyst for alcohol dehydration varies considerably with the method of production of the active material. With hydrated alumina on pumice, ground, screened, and heated at 300° C., Goris [29] concluded that the aldehyde reaction was predominant up to 450° C., below which the ethylene reaction was relatively unimportant but increased rapidly at higher temperature. Several other workers have failed to obtain appreciable decomposition of ethanol to ethylene over alumina at temperatures below 270° C.[30] In contrast to this, Moser obtained yields of 50 to 60 per cent of ethylene over alumina at 250° to 300° C.[31] Other

[27] Ipatiew, *Ber.* **37**, 2986 *et seq.* (1904). *Compare* van Alphen, *Rec. trav. chim.* **49**, 754-61 (1930).
[28] Herndon and Reid, *J. Am. Chem. Soc.* **50**, 3066-73 (1928).
[29] Goris, *Chimie & industrie* 11, 449-52 (1924).
[30] a. Pease and Yung, *J. Am. Chem. Soc.* 46, 2397 (1924); b. Jatkar and Watson, *J. Ind. Inst. Sci.* 9A, 71 (1926).
[31] Moser, *Monatsh.* 44, 141-50 (1923).

workers have also obtained considerable yields of ethylene at these low temperatures. Thus, Kesting [32] claims a yield of 95 per cent over alumina at 400° C. Ordinarily, alumina exerts its maximum activity in the temperature range of 350° to 400° C.[33] for a number of different reactions.

Alumina having strong catalytic action may be prepared by precipitating the aluminum from a one to two per cent aluminum nitrate solution with dilute ammonia. The precipitate is washed by decantation six times, washed on the filter several times, dried over phosphorous pentoxide for 24 hours, heated in an air oven at 240° C., and ground to pass a 200 mesh sieve. After operating for five hours at a temperature close to 500° C. this catalyst showed but a slight decrease in activity.[34] An 80 per cent yield of 98 per cent ethylene was obtained from absolute alcohol at 490° C. When water and alcohol were passed in together somewhat more aldehyde decomposition was obtained.

Alumina in non-vitreous condition may be activated as a dehydrating catalyst by the addition of small proportions of the oxides of the heavy metals of the first, sixth, seventh or eighth group or with compounds of these metals which are convertible into oxides under the conditions of operation.[35]

Sabatier [36] summarized the actions of the catalysts, alumina, titania, and thoria, in the decomposition of ethyl acetate as follows:

$$(Al_2O_3) - 2CH_3COOC_2H_5 = (CH_3)_2CO + 2C_2H_4 + CO_2 + H_2O$$
$$(TiO_2) - CH_3COOC_2H_5 = CH_3COOH + C_2H_4$$
$$(ThO_2) - 2CH_3COOC_2H_5 = (CH_3)_2CO + C_2H_4 + CO_2 + C_2H_5OH.$$
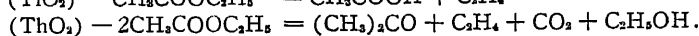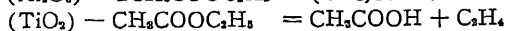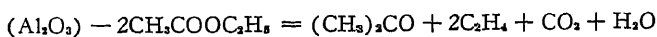
Adkins [37] was unable to confirm these actions experimentally, and concluded that the method of catalyst preparation was of more importance than the particular metallic element present in the catalyst as far as these materials were concerned. The decomposition of the organic compound was not determined by the relative stability of the salts of the acid or alcohol. In the decomposition of ethanol the relative capacities of the catalysts for adsorption of hydrogen or water which was at first used as a basis for explaining the directive capacities of catalysts for either dehydrogenation or dehydration reactions, has been largely abandoned,[38] and a mechanism substituted which postulates a rearrangement of the electrons within the organic molecule so that a split occurs in the molecule. This hypothesis, first advanced by Langmuir,[39] involves the intermediate formation of a compound between the alcohol and the catalyst surface atoms, which compound differs in the case of catalysts of copper and alumina in such a way that the splitting is characteristic of the catalyst material.

[32] Kesting, *Z. angew. Chem.* 38, 362-3 (1925).
[33] Boswell and Dilworth, *J. Phys. Chem.* 29, 1489-1506 (1925).
[34] Engelder, *J. Phys. Chem.* 21, 683 (1917).
[35] French Pat. 679,998 (1930) I. G. Farbenind.
[36] Sabatier, "La Catalyse en Chemie Organique," New York, D. Van Nostrand Co., 1920, p. 341.
[37] Adkins, *J. Am. Chem. Soc.* 44, 385, 2175 (1922).
[38] Taylor, *J. Phys. Chem.* 30, 169 (1926).
[39] Langmuir, *Trans. Faraday Soc.* 17, 617 (1922).

By altering the mode of preparation of alumina catalysts in such a way that the molecular porosity was affected, Adkins [40] has been able to activate preferentially the catalyst for either decarboxylation or dehydration. This was experimentally accomplished by forming aluminum hydroxide and hydrated alumina by precipitation from salts or esters in water or xylene solution and by preparation by the action of water vapor on aluminum 'alk-oxides, pure and supported on pumice. Variation in "ethylene efficiency" from 34 to 150 was obtained in the different catalysts. On the basis of the results, Adkins advanced the hypothesis that molecular porosity of the catalysts determined the directional activity and that large pores favored decarboxylation and small pores dehydration reactions.

'Silica prepared by powdering quartz or decomposing silicon fluoride shows no appreciable catalytic action toward alcohol decomposition.[41] Silica prepared by neutralizing sodium silicate with hydrochloric acid is active and exerts a mixed effect on the decomposition, with the dehydrating tendency predominating. The gas evolved during ethanol decomposition over such a catalyst at temperatures of 380° to 500° C. usually has a composition of 80 to 85 per cent ethylene and 15 to 20 per cent hydrogen.

Zirconia prepared by igniting the nitrate exerts a catalytic action toward accelerating ethanol decomposition but without selective action, since the evolved gas consists of almost equal proportions of ethylene and hydrogen. It is apparently without effect in causing the hydrogenation of ethylene since Engelder obtained no ethane in the gas from the decomposition of either absolute or 50 per cent alcohol.

At temperatures of 320° C. titania, prepared by the dehydration of the hydroxide, is very selective toward dehydration of alcohol. At temperatures of 360° to 400° C., however, it loses its extreme selectivity and a gas containing about 60 per cent ethylene and 40 per cent hydrogen is obtained. When absolute alcohol is used the decomposition may be more selective toward dehydration since it has been shown that the presence of water displaces the decomposition by weakening both the selectivity and the activity of the catalyst.[84] Titania also has the capacity to accelerate the hydrogenation of ethylene, so that quite large amounts of ethane are obtained, especially at temperatures near 400° C. Aldehyde decomposition is not marked and small quantities only of methane and carbon monoxide are obtained. At 490° C. titania causes some decomposition of ethylene with formation of carbon although this is not serious at moderate times of contact. At 520° C. the non-catalytic decomposition of aldehyde is complete, croton aldehyde, methane, ethylene, carbon oxides and some ethane resulting. At 400° C. the decomposition is slight and not as complex as at the higher temperature. In the presence of titania at 400° C. the decomposition is not markedly accelerated nor made more complex.

[40] Adkins. *J. Am. Chem. Soc.* **44**, 2175 (1922).
[41] Sabatier and Mailhe, *Ann. chim. phys.* (8) **20**, 325 (1910).

Thorium nitrate heated suddenly to a high temperature [42] by being dropped into a red hot crucible forms a very light, porous thoria through rapid decomposition. The apparent density is very low, 7.0 grams occupying a volume of 200 cubic centimeters. Because of the enormous surface exposed this catalyst was thought to be a very active one, but on trial was found to be inactive. Apparently, the surface structure is a very important factor in activity. This has been shown in the case of the oxidation catalysts of vanadium pentoxide where very dense, fused material has the highest activity.

Hoover and Rideal [43] have found that thoria prepared by precipitation with ammonia yields approximately equal volumes of ethylene and hydrogen by the decomposition of ethanol contrary to the findings of Sabatier but in agreement with the results of Brown and Reid. [44] Explanations for the dual rôle played by the catalyst surface in promoting the two reactions of dehydrogenation and dehydration of alcohols have been brought forward by various workers and a considerable part of the data available on alcohol decomposition has originated in the work done to support the various theories of catalyst action. In the case of the thoria catalysts for ethanol decomposition, water vapor and acetaldehyde, as poisons, decrease the dehydration reaction to a greater extent than the dehydrogenation reaction. Chloroform in small amounts promotes dehydration and poisons dehydrogenation. Dehydration is also favored by low pressures (1 to 6 mm.). A supported thoria catalyst prepared by heating the nitrate in air promotes the dehydration reaction almost exclusively. This latter effect shows the great importance of the method of catalyst preparation on the activity. A discussion of the different theories that have been offered in explanation of the effects found with such catalysts is too involved for admission here and rightly belongs in treatises on catalytic action. [45] In the case of the catalyst used here the specific surface was evaluated by adsorption of copper ions to be about 23 square meters per gram with about 1.3 per cent of the total surface strongly adsorbing and probably catalytically active. [46]

In the presence of Japanese acid clay ethanol decomposes mainly into ether at 200° C. with formation of only traces of aldehyde and ester. At 300° to 400° C. ethylene is the main product, alcohol and ether being almost absent in the liquid product which comprises 92-96 per cent water. [47a] With a clay catalyst, Hisamura [47b] has obtained a yield of ethylene of 83 per cent in a product that was 98 per cent pure ethylene at 400° C.

Although some of the most effective catalysts have been found to

[42] Kramer and Reid, *J. Am. Chem. Soc.* **43**, 882 (1921).
[43] Hoover and Rideal, *J. Am. Chem. Soc.* **49**, 104 (1927).
[44] Brown and Reid, *J. Phys. Chem.* **28**, 1077 (1921).
[45] For the basis of Rideal's theory *see also* Rideal, "An Introduction to Surface Chemistry," London, Cambridge University Press, 1926.
[46] Hoover and Rideal, *J. Am. Chem. Soc.* **49**, 116 (1927).
[47] a. Kashima, *Bull. Chem. Soc. Japan* **4**, 177-90 (1929); b. Hisamura, *Chem. Abstracts* **18**, 813.

catalyze both dehydrogenation and dehydration, one of these activities may be diminished or suppressed by the addition of suitable "repressers."[48] The addition of basic oxides, hydroxides, etc., of the metals of the first and second groups of the periodic system suppresses the dehydration effect, and the addition of acid oxides, such as those of manganese, sulfur, chromium, phosphorus, arsenic, silicon, titanium, tin, boron, aluminum, or acid salts suppresses the dehydrogenation effect. Thus, when isopropyl alcohol is passed over a zinc oxide catalyst containing 4.5 per cent of sodium carbonate at 400° C., 99 mols of acetone form to every mol of propylene. The substitution of 7 per cent of zinc sulfate for the sodium carbonate results in the production of 60 mols of propylene to every 40 mols of acetone.

' The catalytic dehydration of alcohols proceeds at much lower temperatures in the presence of fused sodium bisulfate than of the aluminum catalysts.[49] Crystalline sodium bisulfate or fused potassium bisulfate are inferior. Ethanol starts to decompose at 175° C. and a maximum yield of ethylene is obtained at 260° C. above which temperature considerable charring occurs. Larger yields of ethylene are obtainable by use of alumina or aluminum salts but the reaction does not start below a temperature of 250° to 270° C. in this case. The fused sodium bisulfate catalyst is efficient in the case of dehydration of the higher alcohols since the lower temperatures that may be used prevent in a large measure the complicating polymerization and condensation reactions that otherwise result. Such strongly acidic catalysts are very active, however, in causing the "cracking" or dissociation of hydrocarbons and at sufficiently elevated temperatures, such as are possible to result from poor temperature control of the reaction, cause the destruction of considerable amounts of the alcohols by breaking down the olefins to carbonaceous matter and hydrogen. For this reason their use is limited even though they are more active toward alcohol decomposition at low temperatures than alumina. Steam may be introduced with the alcohol vapor for the purpose of controlling the action of these catalysts particularly when such highly reactive substances as the diolefins are being formed by dehydrating reactions.[50]

Passage of ethanol vapors over pyro-phosphoric acid at a temperature of 250° to 300° C. results in a 90 per cent yield of ethylene 99.6 per cent pure, no ether and 0.4 per cent of an impurity, possibly a saturated hydrocarbon.[51] Such catalysts exert a powerful polymerizing action on olefins and short times of contact must be used to prevent secondary decompositions. At temperatures of about 150° C. sulfuric acid gives only low conversions to ethylene. Such catalysts as the phosphoric acids and sulfuric acid when used on inert supports for the vapor phase decomposition of alcohols are much more difficult to control in their actions than when

[48] Brit. Pat. 323,713 Marks, assr. to E. I. duPont de Nemours & Co., Inc.
[49] Senderens, *Compt. rend.* 190, 1167-70 (1930).
[50] French Pat. 679,997 (1928) I. G. Farbenind.
[51] Moser and Lindinger, *Monatsh.* 44, 141-50 (1923); *compare* Senderens, *Compt. rend.* 192, 1335-7 (1931).

used in the liquid phase reactions. This is due to the higher temperatures usually used in the vapor phase reactions and the difficulty of maintaining a uniformly moderate temperature throughout the catalyst mass. Vapor phase reactions do, however, permit of more exact control of the time of contact of the reacting substances with the heated catalyst and also permit the better control of such reactions in which a gas is made to react with a vapor in the presence of catalytic material.

The oxides of certain metals of the first, sixth, seventh, and eighth groups of the periodic system, such as copper, chromium, manganese, nickel, cobalt, etc., when deposited on non-vitreous alumina catalyze dehydrogenation reactions. These materials are also active oxidation catalysts and most of the catalysts used today for oxidation reactions occur in these periodic groupings. Hence, the actions of these materials may lead to difficulties in the separation of products because of side reactions which may be set up.[52]

The equilibrium values for the dehydration of ethanol to ethylene have been calculated by Francis[53] and show that ethanol has a considerable tendency to decompose into ethylene.

Apparently, no attempts have been made to determine accurately the equilibria at various temperatures for the dehydration reaction, possibly because of the difficulties involved in the prevention of complicating side reactions which are invariably present in the temperature range involved. Approach to the equilibrium from the hydration of ethylene side is impractical since ethylene has been found to hydrate with considerable difficulty in the vapor phase.* Also, the formation of ethyl ether has been found to occur over a wide range of temperatures and is a complicating factor, especially at the lower temperatures.

The dehydration of the aliphatic alcohols to ethers according to the reaction typified in the case of ethanol by:

$$2C_2H_5OH = (C_2H_5)_2O + H_2O$$

is more of an exception than the general rule when the reaction is conducted in the vapor phase, over active dehydrating catalysts and at relatively high temperatures. Both Sabatier and Ipatiew have reported the presence of ether along with the ethylene obtained by decomposing ethanol over alumina catalysts at temperatures below 250° C. Under laboratory conditions the formation of mixed ethers has been noted when aliphatic and aromatic alcohol mixtures are passed over titania or alumina. Thus, methanol and phenol may result in certain proportions of anisole, $C_6H_5OCH_3$, being formed; and ethanol and phenol in phenetole, $C_6H_5OC_2H_5$.[54]

With anhydrous aluminum sulfate as a catalyst Mailhe and de Godon

[52] *See also* Brit. Pat. 313,425 (1928) I. G. Farbenind.
[53] Francis, a. *Ind. Eng. Chem.* 20, 283 (1928); b. *Proc. Am. Pet. Inst.* XI 93 (1930).
* *Compare* Chapter VII.
[54] Sabatier and Mailhe, *Ann. chim. phys.* (8) 20, 289-352 (1910).

obtained a 71 per cent yield of ethyl ether from ethanol at 190° C.[55] With a catalyst prepared by precipitation of aluminum nitrate with ammonia and ignition, Pease and Yung [56] obtained a 60 per cent yield at 250° C. and a somewhat higher yield at 275° C. Their equilibrium measurements show a maximum possible conversion of ethanol to ether of 62 per cent at 275° C. and 85 per cent at 130° C.[30a] Ipatiew had already shown that the reaction was reversible by obtaining ethanol from equimolar mixtures of ether and water.[27]

Clark, Graham, and Winter have shown that the equilibrium conversion of 66 per cent at 250° C. as shown by calculation from Pease and Yung's data is too low.[57] Using a catalyst prepared by the dehydration of crystalline aluminum hydroxide resulting from the spontaneous decomposition of solutions of sodium aluminate, $(Na_2Al_2O_4)$, these workers obtained a yield of 80.8 per cent ether at 250° C. They also obtained ethanol from equimolal quantities of ether and water showing that the reaction is reversible. They determine the position of equilibrium at 250° C. to correspond to a maximum possible conversion of 85 per cent. The work showed that absolute purity of catalyst was essential. Catalyst impurities were quickly and completely removed by alternately heating to 350° C. and washing. Heating the catalyst to not over 400° C. during drying was found to give the most activity which remained unimpaired even after long use.

These observations have been confirmed by Alvarado,[58a] who obtained yields of 82 per cent ether at 269° C. by using short times of contact. The yield of ethylene is increased, however, by long times of contact showing that secondary decomposition of ether was occurring possibly according to:

$$(C_2H_5)_2O \longrightarrow 2C_2H_4 + H_2O$$
$$(C_2H_5)_2O + H_2O \longrightarrow 2C_2H_5OH.$$
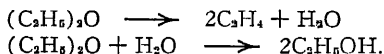
With titania catalysts the action was much less pronounced. Adkins and Perkins,[58b] however, conclude from their work that normally very little of the ethylene formed in the dehydration of ethanol in the presence of alumina is through the ether stage. Ether may also [58c] be prepared by the dehydration of anhydrous ethanol in the presence of aluminum sulfate.

Decomposition under Pressure

Decompositions of alcohol under elevated pressures as well as temperatures were conducted by Ipatiew in a steel autoclave capable of withstanding a pressure of 400 atmospheres.[59] The iron in the apparatus was

[55] Mailhe and de Godon, *Bull. soc. chim.* 25, 565 (1916).
[56] Pease and Yung, *J. Am. Chem. Soc.* 46, 390 (1924).
[57] Clark, Graham and Winter, *J. Am. Chem. Soc.* 47, 2748 (1925).
[58a] Alvarado, *J. Am. Chem. Soc.* 50, 790-2 (1928).
[58b] Adkins and Perkins, *ibid.* 47, 1163 (1925).
[58c] Ger. Pat. 278,777 (1911), Byk.
[59] Ipatiew, *Ber.* 37, 2962, 2983 (1904).

found to catalyze the dehydrogenation of the alcohol and the decomposition of the aldehydes to methane and carbon monoxide.

Comparison of the behavior of alcohol in the presence of an iron catalyst at ordinary pressures and at high pressures showed that in the former case the reaction occurs at a lower temperature and also that for any given temperature the velocity of reaction is much greater.[59] That is, pressure appeared to decrease the decomposition. At ordinary pressures in the presence of an iron catalyst, alcohol decomposes rapidly at temperatures between 510° and 525° C. to give principally acetaldehyde and gases rich in hydrogen. Above 525° C. increases in temperature are accompanied by corresponding decreases in aldehyde production and increases in the quantity of solid carbon deposited on the iron reactor walls.

The observation was made that the pressure developed in the closed apparatus could be made to serve as a fair measure of the decomposition of the substance. By increasing the temperature slowly and studying the effect of temperature upon pressure by means of a series of experiments in which the substance was subjected to the action of heat at various temperatures and during different periods of time the further important observation was made that certain zones of temperature exist within the limits of which a condition of equilibrium seems to prevail between the substance and those of its decomposition products which tend to form at such temperatures. In other words, it may be said that pressure tends to decrease the complete decomposition of the alcohol and to establish regions of temperature and pressure within which a condition of equilibrium is established between it and its decomposition products.

The experimental results showed that the greatest quantity of liquid products were obtained at the lowest temperature at which active decomposition of the alcohol took place. This temperature is relatively higher than the corresponding temperature under ordinary atmospheric pressures. In all cases, the dominating reaction was that of aldehyde formation, although at high pressures the reaction was relatively weaker than at ordinary pressures with the same catalyst. Some ethylene was also always formed, relatively more at ordinary than at high pressures.

Increases in temperature were attended by a rapid falling off in the quantity of the primary liquid oxidation products (i.e. acetaldehyde). This corresponded to an increase in the percentage of saturated hydrocarbons which composed the gaseous decomposition products. Simultaneously the percentage of carbon monoxide increased up to a certain limit and then fell off, the percentage of hydrogen decreased regularly, and the percentage of carbon monoxide varied irregularly. Decreases in carbon monoxide and hydrogen (in the proportion of H_2 and CO) corresponded to increases in the percentage of saturated hydrocarbons. This was accounted for in part on the basis of aldehyde decomposition according to the equation:

$$R.CHO = RH + CO.$$
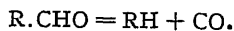
Other factors which might be assumed to contribute to the formation of saturated hydrocarbons under the above conditions are to be found in the tendency of carbon oxides to undergo reduction when heated with hydrogen in the presence of a catalyst. At this time Sabatier and Senderens [60] had already been able to show that both oxides of carbon are readily reduced to CH_4 in the presence of a nickel catalyst at ordinary pressures and Ipatiew therefore assumed that an iron catalyst was capable of activating the same changes in different degrees.

The important observation was made, that at any given temperature, increases in the time of contact (i.e. period of heating) tended to increase the percentage of hydrogen at the expense of acetaldehyde. Thus, for example, the yield of 25 grams of liquid product which was obtained by heating alcohol at 540° C. under a pressure of 226 atmospheres for 95 minutes was decreased to approximately one-half when the substance was heated at the same temperature but slightly higher pressure for 420 minutes. It was also noted as a result of these and other experiments that at very high temperatures complicated mixtures of the higher saturated hydrocarbons were obtained and at the same time the relative percentage of ethylene hydrocarbons was observed to become almost negligible. These changes may be accounted for on the basis of reactions involving hydrogenation of the ethylene. Carbonization, which occurred readily at high temperatures and ordinary pressures in the presence of an iron catalyst, was almost negligible when the heating was conducted under pressure.

Metal catalysts, other than iron, which are known to promote aldehyde decomposition at ordinary pressures exhibit in different degrees the same variations that have just been described when the heating of the substance is conducted under pressure. In general, it may be said that the equilibrium which is established at any given temperature and pressure is to some extent independent of the substance which is used as the starting point of the reaction, since when acetaldehyde is substituted for alcohol, the same gaseous decomposition products are formed in the same relative amounts and the liquid products likewise always consist of aldehyde, alcohol, water, saturated and unsaturated hydrocarbons.

Although ethanol is dehydrogenated to acetaldehyde in the presence of zinc oxide at temperatures of 300° to 400° C. and atmospheric pressure, no aldehyde results when the reaction is conducted under sufficient hydrogen pressure. Instead a complex mixture including esters of acetic, butyric, and caproic acids and alcohols up to and higher than octyl is formed.[61] Condensation reactions of acetaldehyde are used to account for the formation of these compounds but no definite proof has as yet been advanced to establish the mechanisms.

If alcohols, other than methanol, are dehydrogenated under pressure

[60] *Compt. rend.* 134, 514, 689 (1902).
[61] Adkins, Kinsey and Folkers, *Ind. Eng. Chem.* 22, 1046-8 (1930).

in the presence of catalysts composed of cupric oxide containing a few per cent of manganese and magnesium oxides, the character of the product undergoes a marked change. Instead of forming only aldehyde and hydrogen with only small amounts of ester as at atmospheric pressure the decomposition results in a reaction which yields esters as the major product.[62] Consideration of the dehydrogenation reaction will show that pressure should suppress the reaction since it occurs with a volume change of one to two. However, the condensation of aldehydes to esters,[63]

$$2RCHO = RCOOCH_2R$$
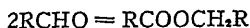
occurs with a volume change of two to one and should be favored by pressure when conducted in the vapor phase. The net effect is for pressure to favor the formation of esters by dehydrogenation of alcohols.

The passage of ethanol vapors over such an activated copper catalyst at one atmosphere pressure and about 350° C. at such a rate that only 50 per cent is decomposed results in the conversion of about 11 per cent of the reacted alcohol to ester and the rest to aldehyde. However, when a pressure of 270 atmospheres is employed and the ethanol conducted over the catalyst at 350° C. at a rate equal to four volumes of liquid ethanol per volume of catalyst per hour, about 50 per cent of the alcohol is converted per pass, 5 per cent is decomposed to carbon monoxide and methane and 45 per cent passes through unchanged. Of the alcohol converted about half goes to ethyl acetate, a quarter goes to form *n*-butyl alcohol, and the remainder forms acetic acid and acetaldehyde. These products are separated by a process of distillation and the hydrogen recovered as such.

Dehydrogenation reactions at atmospheric pressure are endothermic and require a supply of heat. However, it is claimed that under pressure the net heat requirement for the several reactions is less than for those at atmospheric pressure, and that the net effect may even become exothermic.

Other catalysts and combinations have also been claimed for the process. Thus, metals such as copper, cobalt, nickel, iron, either alone, mixed, or with the addition of oxides of other metals as manganese, chromium, magnesium or calcium or mixed oxides which are active synthetic alcohol catalysts as mixtures of oxides of zinc, magnesium, chromium, manganese, etc., are catalysts for the reaction.

In the presence of catalysts such as are used for the synthesis of methanol from mixtures of hydrogen and carbon monoxide and which have been "promoted" by the addition of an alkali oxide, ethanol may be dehydrated to form butanol in a high pressure process. Catalyst mixtures composed of chromium and zinc oxides to which either barium hydroxide or potassium oxide has been added have been specified.[64]

[62] U. S. Pat. 1,708,460 (1928); Brit. Pat. 312,345 (1928) E. I. duPont de Nemours & Co., Inc.; *also* Brit. Pat. 287,846 (1927) to the same.
[63] Tischtchenko, "Beilstein," 4th Ed., Vol. 2, p. 125 (1920).
[64] *Compare* Cryder and Frolich, *Ind. Eng. Chem.* 22, 1051 (1930).

When single metallic oxide catalysts such as magnesium oxide supported on wood charcoal are used at a temperature of 420° to 430° C., a mixture of butanol, ethyl acetate, and aldehyde is obtained from ethanol. When manganese carbonate or zinc oxide supported on wood charcoal is used at 450°, ethanol decomposes into only butanol and aldehyde.[65]

Reduction of Acetaldehyde

The fact that the dehydrogenation of alcohols to aldehydes and ketones was a reversible reaction was recognized by Ipatiew. The hydrogenation of the lower members of the aliphatic series of aldehydes in the vapor phase has been investigated by Sabatier and Senderens [66] and more recently by Armstrong and Hilditch [9] and by Negoshi.[67] In the earlier investigations the best results were obtained by using a nickel catalyst (prepared by reducing the oxide or hydrate precipitated upon a suitable carrier) and the reaction is described as taking place very smoothly at temperatures slightly above the boiling point of the alcohol (i.e. 80° C.). When carried out at 140° C., yields approximating 80 per cent alcohol are described as having been obtained.[68] No by-products were formed and the alcohol which contained small quantities of aldehyde was readily rectified. The reaction was favored by the use of pure aldehyde free from water. The same reaction was found to take place in the presence of cobalt at 180° C., but this catalyst was much less effective. Finely divided copper was not found to be a practical catalyst for this reaction, according to Sabatier, because of the fact that it does not induce the reaction below a temperature of 200° C., at which temperature acetaldehyde tends to decompose into methane and carbon monoxide although it was known to promote the reverse reaction,

$$C_2H_5OH = CH_3CHO + H_2$$

at temperatures between 200° and 330° C.[69] Finely divided platinum was also found to be impractical for much the same reasons.

In repeating the work of Sabatier and Senderens, Armstrong and Hilditch found that at temperatures between 120° and 150° C. a transformation to 53.6 per cent alcohol was effected in the presence of finely divided nickel. When a copper catalyst was used a yield of 87.5 per cent alcohol was obtained at 200° to 210° C. This yield was decreased to 33.7 per cent at 300° C., at which temperature a great increase in the gaseous decomposition products was observed. The reverse reaction:

$$CH_3CH_2OH = CH_3CHO + H_2$$
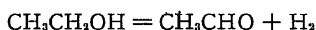
yielded 35.7 per cent aldehyde in the presence of a nickel catalyst at 240° to 260° C., and as high as 92 per cent aldehyde in the presence of copper

[65] French Pat. 645,169 (1927) Consortium für Elektroch. Ind.
[66] a. *Compt. rend.* **137**, 301 (1903). *Also compare* b. Sabatier-Reid, "Catalysis in Organic Chemistry," New York, D. Van Nostrand Co., Inc., 1922, p. 432, 503, 522, 532.
[67] Negoshi, *Repts. Imp. Ind. Res. Inst. Osaka, Japan* **5**, 1-361 (1924).
[68] G. Mignonac, *Bull. soc. chim.* **29**, 465 (1921).
[69] *Compt. rend.* **136**, 738 (1903).

at 295° to 300° C. The presence of water vapor was thought to protect the aldehyde from hydrogenation and so to increase the yields. Negoshi in working with a nickel catalyst which was prepared by soaking pumice in 30 per cent nickel nitrate solution and then heating at 500° C. in a stream of hydrogen for six hours found that the reduction of aldehyde could be effected at 140° C. with yields of alcohol as high as 90 per cent. When the nickel was prepared by reducing the oxide, the same reaction was found to take place at temperatures as low as 100° C., provided that a thirty fold excess of hydrogen was present. The equilibrium relations represented by:

$$CH_3CHO + H_2 \rightleftharpoons CH_3CH_2OH$$
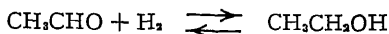
have also been studied in the presence of cerium oxide at temperature ranges of 300° to 380° C.[70]

That ethanol may exhibit the same rôle as water in protecting the aldehyde from decomposition is shown by comparing the results of the hydrogenation and dehydrogenation reactions at 300° C. and in the presence of copper catalysts. When ethanol is decomposed under these conditions very little methane and carbon monoxide are produced and high ratios of aldehyde to hydrogen are obtained showing that little aldehyde is decomposed. On the other hand, when the aldehyde is being reduced in the presence of excess hydrogen but with little alcohol present at temperatures as low as 250° C. much of the aldehyde is decomposed.[71] Whether this is entirely a matter of protective action or whether the time of contact at actual measured temperatures can account for the differences cannot be said on the basis of the published results.

In operations on a commercial scale both nickel and copper have been applied to the production of alcohol from acetaldehyde.[72] In the manufacture of ethyl alcohol by passing the vapor of acetaldehyde mixed with hydrogen over a nickel catalyst, the product is always more or less contaminated by the presence of unreacted acetaldehyde. This may, however, be reduced to a small fraction if hydrogen is used in large excess as compared with the quantity theoretically required for the reaction. To avoid the loss of hydrogen through leakage, etc., the principle of circulation is applied to the operation. This arrangement still further favors the production of alcohol if the excess of hydrogen is kept high enough to remove the heat of the strongly exothermic reaction sufficiently to maintain a temperature of 100° to 180° C. within the reaction chamber. How great this excess should be in any particular case may be calculated (a) from the quantity of heat developed per unit of time, (b) from the heat lost by radiation and general external cooling and (c) from the heat capacity of the hydrogen between the ranges of temperature (i.e. 100° to 180° C.)

[70] Milligan and Reid, *J. Am. Chem. Soc.* 44, 202 (1922).
[71] Palmer, *Proc. Roy. Soc.* 98A, 13 (1920).
[72] a. Swiss Pat. 74,129 (1917) Elektrizitatswerk Lonza; b. Brit. Pat. 120,163 (1918) Bloxam, assr. to Elektrizitatswerk Lonza; c. Brit. Pat. 134,521 (1919) Elektrizitatswerk Lonza; *also, compare* d. U. S. Pat. 1,408,749 (1922) Lichtenhahn, assr. to Elektrizitatswerk Lonza.

permissible within the apparatus. Ordinarily a threefold excess is found to be desirable. The alcohol may be separated by condensing the issuing vapor and the hydrogen returned to the apparatus by means of an external circulation device, or by means of an injector.

In manufacturing alcohol by means of the process which has just been described it was found that the yield depended upon the exclusion of oxygen, water, and of acetic acid. But when oxygen was completely excluded the alcohol was found to contain small quantities of ether, the presence of which is objectionable for certain uses. Moreover, when a large excess of hydrogen was circulated during the process, certain impurities such as methane, carbon monoxide and dioxide were formed. Of these carbon monoxide was injurious to the catalyst, its activity decreasing rapidly in proportion to the amount of carbon monoxide formed. It was then found that both of these objectionable features could be avoided by adding oxygen gas up to 0.3 per cent to the mixture of acetaldehyde and hydrogen. Under these conditions ether was no longer produced and the decrease in the activity of the contact body due to the presence of carbon monoxide was practically eliminated. It is interesting to note that the formation of water during the combustion of the oxygen is not in itself responsible for the favorable effect. Nor is the oxidation of carbon monoxide to dioxide, since the addition of 0.05 per cent oxygen served to counteract the poisoning effect caused by the deliberate addition of 0.1 per cent carbon monoxide. In other words, there was an unexpected and unexplained typical action of oxygen. According to these later specifications a temperature range of 90° C. to 170° C. is desirable because below 90° C. the formation of alcohol is slow and above 170° C. the decomposition of acetaldehyde increases rapidly. Yields of alcohol up to 95 per cent were obtained with an aldehyde content of 0.07 per cent and an ether content of 0.5 per cent. The action of the small amounts of oxygen required for maintaining the catalyst activity is explainable on the basis of catalyst activation, possibly through a process of oxidation and reduction.

Finely divided copper prepared by precipitation from a salt solution with alkali followed by reduction in hydrogen at 200° C. is active as a hydrogenating catalyst at 180° C. A relatively wide variation in range as well as a fairly high reaction temperature are said to be practical if a corresponding velocity in the gas flow is maintained, but it is, in general, desirable to keep the temperature inside the reaction chamber between 150° and 200° C.[73] Copper is said to possess certain advantages over a nickel catalyst because it is cheaper and because of the fact that it will not deteriorate by oxidation within the range of temperatures prescribed for the reaction.[74]

Copper in other forms may also be used as a catalyst.[75] For example,

[73] Negoro, *Repts. Imp. Ind. Res. Inst. Osaka* 7, 10, 1-23 (1926).
[74] Swiss Pat. 93,277 (1922); Ger. Pat. 350,048 (1920); Brit. Pat. 158,906 (1922); and U. S. Pat. 1,410,233 (1922) Badische Anilin u. Soda Fabrik.
[75] Swiss Pat. 94,603 (1922); Ger. Pat. 362,537 (1921); Brit. 175,238 (1922) Badische Anilin u. Soda Fabrik.

pumice saturated with copper formate and then heated at 200° to 250° C. may be employed; or malachite in coarse pieces may be reduced at 200° to 250° C.; or so-called natural copper or any form of copper powder, mixed with water glass or colloidal silicic acid or other activators may be deposited on pumice, oxidized at 200° C. and reduced again at 250° C. In general, copper obtained from a great variety of compounds by the use of many different reagents may be employed for the reduction of acetaldehyde by hydrogen at temperatures of 150° to 200° C. So long as the copper compounds are not heated above 350° C. during the process and are subsequently reduced at relatively low temperatures, the efficiency of the copper remains unimpaired.

Although alcohol has been produced by the hydrogenation of acetaldehyde obtained from the hydration of acetylene, this source is relatively unimportant ordinarily. It does, however, furnish a means for the synthesis of ethanol from such sources of carbon as calcium carbide, methane, the carbon arc, etc., which might become of importance during periods of war, or in locations where very cheap electric power is available. Experiments on a technical scale [76] in Switzerland have shown the process to be successful but at a cost too high to make the process competitive.

Although the vapor phase reduction of aldehyde to ethanol is a reaction which occurs with a change of volume of two to one and should be markedly influenced by the application of pressure, very little work has been reported in the literature to show this effect. It is probable that the use of considerable excesses of hydrogen will be necessary to prevent the condensation reactions of the aldehyde which also occur with decrease in volume. Processes have been claimed for the synthesis of esters by such condensation reactions:

$$2CH_3CHO = CH_3COOC_2H_5$$
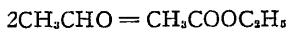
which are conducted in the presence of catalysts such as aluminum ethylate, aluminum chloride, or metallic aluminum.[77]

Acetaldehyde may also be used for the preparation of normal butanol by passing it first over the oxides of thorium, titanium, or uranium at a temperature of 360° C. and then reducing the crotonic aldehyde which is thus formed by passing the issuing gases over reduced nickel.[78]

Formation of Carbon Dioxide from Alcohol Decomposition

Under certain circumstances carbon dioxide is evolved during the decomposition of alcohols over catalysts. For instance, the gaseous products contain 1.5 to 3.5 per cent carbon dioxide when ethanol is decomposed in the presence of titania at 430° C., 1 to 2 per cent when butanol

[76] *Compare* Hilditch, "Catalytic Processes in Applied Chemistry," London, Chapman and Hall, 1929, p. 298.
[77] a. Petrenko-Kritschenko, *J. Russ. Phys. Chem. Soc.* 33, 260 (1901); b. Brit. Pats. 26,825, 26,826 (1913); Ger. Pats. 314,210 (1914), 386,688 (1921) Consortium f. Elektrochem. Ind.
[78] a. Sabatier, *Compt. rend.* 166, 632 (1918); *compare* b. Komatsu, *J. Chem. Soc.* 1A, 1924, p. 1042.

is decomposed under the same conditions, upwards of 5 per cent when ethanol is decomposed over zinc oxide catalysts prepared from zinc isopropoxide, and less than 1 per cent under the same conditions when zinc oxide from zinc hydroxide is the catalyst.[79]   As much as 10 per cent carbon dioxide has been found when ethanol is decomposed over a copperchromium catalyst at 500° C. (*see* Fig. 4).[80]   In all cases where carbon dioxide has appeared in appreciable amounts in the gaseous reaction product there have been evidences of a brown, odorous, unsaturated oil or resinous material.

Various explanations have been offered for the mechanism of the formation of the carbon dioxide and of the ethane which has also been obtained in certain cases.   None of these are entirely free from objections.   Aldehydes are known to condense to esters under certain conditions and the decarboxylation of such has been offered as one explanation.   However, the presence of carbon dioxide by this mechanism has not been supported by the evidence of other products of ester decomposition.   Methane formation has not been reported in all cases where carbon dioxide has been found and this, together with the fact that entirely inadequate amounts of carbon have been found, seems to point that the rupture of acetaldehyde to $C + CO_2$ instead of carbon monoxide does not occur.   The decomposition of aldehyde alone in the presence of precipitated iron oxide at 400° C. gave 40 per cent carbon dioxide and a large quantity of resinous matter.[79]   In the presence of reduced nickel, however, no carbon dioxide was formed

Fig. 4.—Composition of the gases from the decomposition of ethanol in the presence of supported copper-chromium catalysts.[80]

and no resinous matter or oil resulted although nickel is an active catalyst for aldehyde decomposition.

It is possible that the dehydrogenation of aldehyde to ketene, as in the well known case with acetone, and the subsequent reaction of ketene and aldehyde to give carbon dioxide and an unsaturated hydrocarbon is the explanation.[79]   The presence of acetic acid might also be accounted for by the interaction of ketene and water.   No such reaction would be expected in the case of isopropanol since a temperature of 650° C. is required for the formation of ketene from acetone and only traces of carbon dioxide have been reported from this alcohol.[81]

The presence of ethane in ethanol decomposition has been accounted for by Engelder [82] by the hydrogenation of ethylene over catalysts that

[79] Adkins and Lazier, *J. Phys. Chem.* 30, 895 (1926).
[80] Boomer and Morris, *Can. J. Research* 2, 384-7 (1930).
[81] *Compare* with the following on ketene reactions: a. Schmidlin and Bergman, *Ber.* 43, 2821 1910); b. Hurd and Kucour, *J. Am. Chem. Soc.* 45, 2170 (1923).
[82] Engelder, *J. Phys. Chem.* 21, 676-704 (1917).

have both dehydrating and dehydrogenating actions. Adkins, however, has proposed [83] the reaction:

$$2C_2H_5OH = C_2H_6 + CH_3CHO + H_2O$$
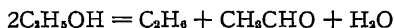
to account for the ethane. From their results (Fig. 4) Boomer and Morris suggest that the reaction proposed by Adkins is the logical one. They do not, however, attempt to explain the large amounts of carbon dioxide, the small amount of brown oil, the acid nature of the condensate, and the absence of carbon deposits obtained in the decomposition of ethanol over their silica gel supported copper-chromium catalyst.

Summary of Ethanol Decomposition

The work on the decomposition of ethanol over various catalysts has been reviewed in some detail, not only because it serves to show that any one of three major routes may be induced and controlled by means of variation in temperature, pressure, and choice of catalyst, but also because it helps to demonstrate that even at comparatively low temperatures these reactions are always accompanied by secondary or side reactions. In summary, it may be said that unnecessarily high temperatures are to be avoided since the yields of the various products, aldehydes, ethers, and olefins, rapidly decrease and these products are replaced by the more or less complicated mixtures of hydrocarbons and oxygenated compounds due to decompositions, polymerizations and the large number of side reactions possible between the various decomposition products. For example, acetaldehyde decomposes to give methane and carbon monoxide; ether to give ethylene and water; ethylene polymerizes to give higher olefins. Hydrogen may react with the oxides of carbon to give methane, or with ethylene to give ethane. The saturated hydrocarbons may in turn undergo dissociation and subsequent polymerization. To understand the rôle which these various side reactions play in the pyrogenic decompositions of alcohol, each such reaction needs to be considered separately with a view to determining its particular equilibrium relationships and thermodynamics. Progress in a knowledge of catalysis has fortunately been accompanied by the accumulation of data of this kind some of which will be discussed in later sections of this book.

Decomposition of the Higher Alcohols

Acetone which was formerly made almost exclusively by the dry distillation of calcium acetate obtained in the destructive distillation of wood, is now made on a large scale by the dehydrogenation of isopropyl alcohol obtained largely from the hydration of propylene contained in refinery gases.[84] The other remaining sources of acetone at present are the wood distillation industry, the fermentation process of butanol manufacture,

[83] Taylor, *J. Phys. Chem.* 30, 145-171 (1926).
[84] *Compare* Baldwin, *J. Soc. Chem. Ind.* 49, 51T (1930); Brit. Pat. 337,566 (1929) Elkington, assr. to N. V. de Bataaf, Pet. Maats.

by the decomposition of acetic acid or acetates, largely synthetic. Although no description of the details of the dehydrogenation process have been published for the commercial process, some data are available from laboratory experiments.

In general, as has been shown by the work of Sabatier and Senderens, it is apparent that at any given temperature and with any given catalyst the rate of decomposition is much greater for secondary than for primary alcohols, and that increases in temperature produce a more rapid increase in rate for the former than for the latter class of compounds.

In the presence of finely divided active copper, such as has been used in the dehydrogenation of ethanol, isopropyl alcohol readily forms acetone and hydrogen. At 300° C. the equilibrium is well over toward the acetone

$$\begin{matrix} CH_3 \\ CH_3 \end{matrix} > CHOH = \begin{matrix} CH_3 \\ CH_3 \end{matrix} > CO + H_2$$
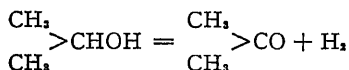
side.[85] A number of patents have been taken out for processes conducted in the presence of copper or brass either with or without air.[86]

Normal propyl alcohol is readily dehydrogenated to the corresponding aldehyde at temperatures of 230° to 300° C. in the presence of copper catalysts. At temperatures of 400° C. as much as 25 per cent may be destroyed, however, by decomposition to carbon monoxide and ethane. In the presence of nickel 75 per cent of the aldehyde may be decomposed at a temperature as low as 260° C. Although the alcohol is dehydrogenated very readily over platinum at 280°, the aldehyde is completely destroyed at 300° C.*

The losses by secondary decompositions are far less in the case of the dehydrogenation of secondary than in the case of the primary alcohols due to the greater stability of the ketones compared with the aldehydes. Thus, in the presence of platinum the destruction of acetone amounts to only 3 per cent at 400° C. when isopropyl alcohol is decomposed.

Isopropyl alcohol is dehydrated to propylene and water by the same type of catalysts that are effective with ethanol. Because of the higher original molecular weight of the alcohol, however, somewhat more complex decompositions are possible, especially at excessively high temperatures or in the presence of very active catalysts. At temperatures of 300° to 350° C. the main products are propylene and water when active dehydrating catalysts as alumina, titania, or clay are used.[87, 47a,] *

Fused sodium bisulfate is an effective catalyst for the dehydration of the aliphatic alcohols.[88] Normal propyl alcohol is dehydrated at 125° to

[85] Parks and Kelley, *J. Phys. Chem.* 32, 740 (1928).
[86] a. U. S. Pat. 1,460,876 (1923) Williams and White; b. U. S. Pat. 1,541,545 (1925) Wells; c. U. S. Pat. 1,487,817 (1923) Wells; d. Brit. Pat. 173,539 (1920) Hunt.
* *See* p. 650 *et seq. ref.*, 66b.
[87] a. Allardyce, *Trans. Roy. Soc. Can.* (3) 21, Sect. 3, 315-21 (1927); b. Peytral, *Bull. soc. chim.* 35, 960 (1924); c. Dohse and Kalberer, *Z. phys. chem.* 5B, 131 (1929).
[88] Senderens, *Compt. rend.* 190, 1167-70 (1930).

140° C., isopropyl begins to lose water at 95° C. and decomposes rapidly at 105° to 110° C., and isobutyl alcohol is dehydrated at 135° C.

When dehydrated in the presence of acidic catalysts as phosphorous pentoxide, phosphoric acid, or sulfuric acid at temperatures below 160° C., both 1-butanol and 2-butanol gave a mixed 2-butene free from 1-butene.[89] Phosphoric acid did not attack 1-butanol under the conditions. With phosphoric acid on pumice, aluminum phosphate, or aluminum oxide as catalyst 2-butanol decomposed largely to 2-butene with small amounts of 1-butene. The decomposition of 1-butanol to 1-butene over these three catalysts increased in the order named, reaching 73 per cent in the presence of alumina.[90, 47]

Normal butyl alcohol may be dehydrogenated to give a mixture consisting of butyric aldehyde, butyl butyrate, hydrogen, and unreacted alcohol by passing the vapors preheated to 125° C. through tubes containing a fused cupric oxide catalyst [91] and heated to 280° to 300° C. by immersion in a liquid bath. Hydrogen is recovered from the condensed liquids and about 500 pounds of the ester is formed from every 6600 pounds of alcohol treated.[92]

1-Butanol is vaporized and passed over a copper catalyst [93] for the purpose of dehydrogenation to aldehyde. The aldehyde is separated from the products by fractionation and oxidized to butyric acid in the liquid state with air or oxygen in the presence of a catalyst such as manganese butyrate. With a copper tube ¾ inch in diameter and packed for 26 inches with fused cupric oxide 240 cc. of butanol per hour may be treated with a 75 per cent conversion per pass.[94] At temperatures of 220° to 280° C. the yields of aldehyde are good. At 370° C. only about one-sixth of the aldehyde that forms is decomposed.

In the presence of nickel 2-butanol begins to decompose at 160° C., and yields butanone readily at 300° C. without formation of butylene.

Isobutyl alcohol is readily transformed into the corresponding aldehyde at 240° to 300° C. in the presence of copper. About one-half of the aldehyde is destroyed, however, when the operating temperature is raised to 400° C.

Over copper isoamyl alcohol yields the aldehyde at 240° to 300° C. without side reactions. About 6 per cent of the product is decomposed at 390° C. and about 25 per cent at 430° C.

Tertiary alcohols are readily dehydrated to form olefins. The velocity

[89] a. Young and Lucas, *J. Am. Chem. Soc.* **52**, 1964-70 (1930); b. King, *J. Chem. Soc.* **115**, 1404 (1919).
[90] *Refer also to* a. Le Bel and Green, *Bull. soc. chim.* **35**, II, 438 (1881); b. Brown and Reid, *J. Phys. Chem.* **28**, 1081 (1924); c. Lepingle, *Bull. soc. chim.* **39**, 741 (1926); d. Coffin and Maass, *J. Am. Chem. Soc.* **50**, 1427 (1928); e. Davis, *ibid.* **50**, 2769 (1928); f. Lucas, Dillon and Young, *ibid.* **52**, 1949 (1930).
[91] U. S. Pat. 1,401,117 (1921) Commercial Solvents Corpn. (Catalyst).
[92] U. S. Pat. 1,580,143 (1926) Commercial Solvents Corpn. (Process).
[93] Brit. Pat. 166,249 (1920) Adam (Catalyst).
[94] a. Brit. Pat. 173,004 (1920) Adam; b. U. S. Pat. 1,418,448 (1922) Legg, assr. to Adam.

of decomposition over alumina or bauxite increases from the normal through the secondary to the tertiary alcohol in the case of butanol.[95]

In the presence of reduced nickel, acetone is reduced to isopropyl alcohol at 210° to 220° C. At 200° to 230° C. isopropyl alcohol is dehydrogenated in the presence of nickel and also begins to decompose into saturated hydrocarbons. Under pressure an equilibrium between these two reactions is established. At 250° C. the approach to equilibrium is very slow and is accompanied by decomposition of both acetone and isopropyl alcohol into gaseous hydrocarbons.[96] For normal secondary butyl alcohol the corresponding temperatures are somewhat higher, being about 250° to 300° C. in the presence of reduced nickel. The higher

$$\begin{array}{c} CH_3 \\ C_2H_5 \end{array}\!\!>\!\!CHOH \rightleftarrows H_2 + \begin{array}{c} CH_3 \\ C_2H_5 \end{array}\!\!>\!\!CO.$$
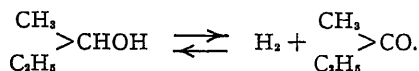
primary alcohols require relatively higher temperatures for decomposition than the corresponding secondary alcohols.

In general, iron as a reducing catalyst requires a higher temperature than nickel. Reactions requiring temperatures of 200° to 230° C. with nickel catalysts do not occur at comparable rates over iron until a temperature of about 400° C. is reached. At 300° C. isopropyl alcohol tends to decompose into water and saturated hydrocarbons over nickel catalysts. A temperature of 570° C. is required for the same decomposition over iron. This tendency for nickel to decompose the alcohols into saturated hydrocarbons makes its use for the conversion of alcohols into aldehydes and ketones difficult from an industrial standpoint.

Excellent data are available for comparison of the actions of different aliphatic alcohols in the presence of different catalysts but under comparable conditions from the work of Adkins and his coworkers[97] on catalysts.

The temperature effect on the dehydration of alcohols in the presence of alumina as has been shown by the work of Sabatier and Mailhe,[41] Brown and Reid,[90b] and Pease and Yung[98] was not checked by Adkins,[97b] who used what were presumably better conditions experimentally. The rate of dehydration increases in the order of butyl, propyl, isobutyl, ethyl, isopropyl, and secondary butyl alcohols. Although ethanol and ethyl ether give the same rate of dehydration, butyl alcohol gives a faster dehydration rate than does butyl ether. Hence, the hypothesis advanced at one time that olefin formation from alcohols was through intermediate ether formation cannot hold.

In the presence of zinc oxide catalysts prepared by precipitation from a zinc sulfate solution the proportion of dehydration and dehydrogenation

[95] Dohse, *Z. physik. Chem.* **6B**, 343 (1930).
[96] Ipatiew, *Ber.* **40**, 1270 (1907).
[97] Adkins, Perkins, Lazier, Bischoff, and Nissen, a. *J. Am. Chem. Soc.* **44**, 386, 2175 (1922); **45**, 809 (1923); **46**, 130, 2291 (1924); **47**, 808 (1925); b. *ibid.* **47**, 1163 (1925); c. *ibid.* **47**, 1719 (1925); d. *ibid.* **48**, 1671 (1926).
[98] Pease and Yung, *J. Am. Chem. Soc.* **46**, 402 (1924).

is constant over the temperature range of 350° to 440° C. for the four primary alcohols studied. Although small amounts of carbon oxides were formed the results of experiments were reported as though hydrogen and olefin constituted 100 per cent of the decomposition. For primary alcohols these results were:

Ethanol	9.5% ethylene	90.5% hydrogen
n-butanol	15.0% butylene	85.0% hydrogen
n-propanol	16.0% propylene	84.0% hydrogen
isobutanol	31.5% butylene	68.5% hydrogen

Temperature, however, has a marked effect on the proportions of the two competing reactions in the case of the secondary alcohols as is shown in the following results:

isopropanol:

345° C.	89% propylene	11% hydrogen
394° C.	80% propylene	20% hydrogen
418° C.	71% propylene	29% hydrogen

secondary butanol: ·

345° C.	88% butylene	12% hydrogen
377° C.	79% butylene	21% hydrogen
398° C.	75% butylene	25% hydrogen
418° C.	73% butylene	27% hydrogen

The alcohols showed about the same relative reactivity over zinc oxide as over the alumina catalyst.

A comparison, however, of zinc oxide catalysts prepared in different ways, i.e. (A) precipitation of zinc hydroxide from zinc sulfate, (B) "dry process" commercial zinc oxide, and (C) hydrolysis of zinc isopropoxide in moist air, showed that the mode of preparation had a marked effect on the catalyst action. The percentage of olefin formed at a given temperature varied from 5 to 88 for isopropanol, 10 to 20 for ethanol, 1 to 31.5 for isobutanol, and 2 to 15 for *n*-propanol and butanol. In general, catalyst A was best for dehydration, and catalyst B for dehydrogenation, except in the case of ethanol where they were about the equal. Catalyst C behaved about the same as B, except in the case of ethanol, in which case it was a better dehydration material.

SUPPLEMENTARY REFERENCES

1. Hurd, "The Pyrolysis of Carbon Compounds," (1929), New York, Chemical Catalog Co., Inc., 1929, pp. 148-197 (the pyrolysis of alcohols); pp. 198-231 (the pyrolysis of ethers); pp. 236-247 (the pyrolysis of aldehydes).

Chapter III

Oxidation of Alcohols to Aldehydes and Acids

Oxidation with Molecular Oxygen

Prior to 1916, acetaldehyde was manufactured by the oxidation of alcohol in the liquid phase with bichromate and sulfuric acid.[1] Since that time it has been made quite largely by the hydration of acetylene in sulfuric acid solutions activated with mercury salts. However, the relatively low price of ethanol in America has made the formation of acetaldehyde by vapor phase dehydrogenation or limited oxidation of the alcohol attractive commercially. To this end several methods have been proposed for conducting the transformation industrially. Developments of processes employing vapor phase oxidation reactions have all been based largely on the principles disclosed by the early work, a considerable portion of which had been undertaken purely for the purpose of research and not industrialization.

The pyrogenic decomposition of alcohols over certain directive catalysts to form aldehydes and ketones, as has been shown in the preceding chapter, results from the splitting out of hydrogen. Since the dehydrogenation of alcohols is a reversible reaction, the removal of hydrogen from the scene of the reaction results in the more complete decomposition of the alcohol with higher yields of aldehydes and ketones. The use of oxygen as air or in special gas mixtures to react with the evolved hydrogen to form water in the presence of certain catalysts has resulted in the adoption of the process for the industrial production of aldehydes and ketones. The heat evolved by the combustion of the hydrogen also helps to maintain the proper temperature in the reactor and may eliminate the necessity for adding heat. The selection of catalysts that are directive to both dehydrogenation and oxidation has been the goal of a large proportion of the research devoted to this problem. Since continued oxidation may result in the formation of acids and ultimately of carbon oxides and water, it has been necessary to restrict the proportion of oxygen to alcohol, control the temperature of oxidation by admixture of steam, or make a careful choice of catalysts that are not too active, in order that maximum yields of the desired products may be realized.

In following the development of the process it is desirable to consider methanol oxidation separately since it presents problems that are unique.

[1] Ullmann, "Enzyklopädie der technischen Chemie," Second Ed., pp. 95-99.

Consequently, alcohols of the aliphatic series other than methanol will be considered here.

The earliest references to the oxidation of these substances are to be found among the researches of Sir Humphry Davy,[2] who observed that a platinum spiral when slightly heated and introduced into a mixture of air and a combustible gas becomes incandescent and that this phenomenon is accompanied by the slow combustion of the gas. A few years later Edmond Davy [3] made the further discovery that platinum black possessed the power to ignite alcohol when moistened with it. In 1893 Kuhlmann [4] in connection with his studies on the oxidation of ammonia, observed that vapors of alcohol when mixed with air may be oxidized to acetic acid by passing them through a hot tube containing spongy platinum. Following this discovery, the action of platinum in various forms was made the subject of more or less extended but rather poorly conducted investigations. Thus, Strecker [5] and somewhat later Grimaux [6] found that alcohols could be oxidized to aldehydes and even to acids by the action of platinum black. The results obtained from these experiments were very irregular because of the fact that the catalytic effect of the particular modification of platinum used was very violent and was prone to cause explosions, particularly at the beginning of the reaction. At about the same time Hofmann [7] and Tollens [8] succeeded in preparing formaldehyde by passing the vapors of methanol mixed with air over a weakly glowing platinum spiral. In the course of his investigations Tollens made the further observation that mixtures of methanol and oxygen exploded when in contact with a large number of other metals heated to redness and that copper in particular possessed much the same properties as platinum as an oxidizing catalyst and may be substituted for it. In subsequent experiments air was conducted through methanol, heated at 45° to 50° C. on a water bath, and the mixed vapors sucked through a hot tube containing either a platinum spiral or cylinder of copper gauze in 5 cm. lengths. Tollens found that the percentage yield of aldehyde depended upon the temperature of the water bath or, in other words, upon the proportions of methanol and air, viz.,

Temperature of Liquid Methanol ° C.	Yield of Formaldehyde Per Cent
22 to 32	17.95
38 to 40	28.9
48 to 50	31.5

The form of copper used in this work was such that the initial temperature of the reaction was much higher than when platinum was used.

[2] Humphry Davy, *Phil. Trans.* **97**, 45 (1817).
[3] Edmond Davy, *Schweiggers J.* **34**, 91 (1822); **38**, 321 (1823).
[4] Kuhlmann, *Ann.* **29**, 286 (1839).
[5] Strecker, *Ann.* **93**, 370 (1855).
[6] Grimaux, *Bull. soc. chim.* (II) **45**, 481 (1886).
[7] Hofmann, *Ann.* **145**, 357 (1868); *Ber.* **2**, 152 (1869); **11**, 1685 (1878).
[8] Tollens, *Ber.* **15**, 1629, 1828 (1882); **16**, 917 (1883); **19**, 2133 (1886).

However, no data as to optimum temperatures or times of contact were given. Loew [9] in continuing the study of the oxidation of methanol confirmed Tollens in the feasibility of substituting copper for platinum as a catalyst and obtained somewhat higher yields of aldehydes. Kablukow [10] is also to be associated with Tollens and Loew in attempting to modify Hofmann's experiments in such a way as to facilitate the preparations of formaldehyde in relatively large quantities.

All of these investigations were conducted in the presence of excess air with the result that the yields of aldehyde were small since varying quantities of the reacting compounds were completely oxidized.

This period of more or less preliminary investigation was followed by one marked by a much greater effort toward accuracy in defining the precise conditions for each experiment. Trillat [11] and Orloff,[12] whose individual research will be discussed more fully in a later chapter dealing specifically with the oxidation of methanol to formaldehyde, were most conspicuous in forwarding these developments. It may be stated in brief at this point that the same catalysts were, in general, employed by these investigators as have already been described, namely, platinum in its various forms of aggregation, copper and zinc, and bodies such as glass or porcelain impregnated with the oxides of copper, manganese, iron, lead, silver or gold. In his early work Trillat performed a series of experiments with different primary alcohols in which he passed a mixture of air and the vapor of the alcohol over a platinum spiral heated to redness. The results of these experiments may be summarized as follows: The corresponding aldehydes which were always formed, represented from 1.8 to 1.5 per cent of the alcohol used. The presence of water vapor did not appear to influence the oxidation. Methanol and ethanol also yielded methylal and acetal respectively. The latter reaction is reversible since on passing the vapor of either of these acetals over a platinum spiral, the aldehyde and alcohol are regenerated, a decomposition which is accompanied by a sufficient development of heat to render the spiral incandescent. The platinum also catalyzes the hydrolysis. When methylal and water vapor are passed over the catalyst formaldehyde and methanol are produced. In the presence of platinum black, the alcohols were oxidized to the corresponding acids. Besides the lower alcohols Trillat experimented with propyl, isopropyl, butyl, isoamyl, heptyl and primary octyl alcohols. In later operations the device of electrical heating by passing a current of electricity through the catalyst spiral was made use of. This work was inaccurate, largely because of the fact that the heat generated in the platinum was due to successive explosions and not to a steady reaction temperature maintained over a long period of time. It also possessed the

[9] Loew, *J. prakt. Chem.* **33**, 324 (1886); *Ber.* **20**, 141 (1887); *Ber.* **23**, 289 (1890).
[10] Kablukow, *J. Russ. Phys. Chem. Soc.* **14**, 194 (1882).
[11] Trillat, *Bull. soc. chim.* (3) **27**, 96 and 797 (1902); *ibid.* (3) **29**, 35-47 and 939 (1903); Brit. Pat. 8575 (1895); *Compt. rend.* **122**, 482 (1896); **132**, 1227 and 1495 (1901); **137**, 187-9 (1903); Ger. Pat. 55,176 (1891) and 81,023 (1894).
[12] Orloff, "Oxidation des Alcools par L'Action de Contact," Paris, 1901.

disadvantage of being qualitative rather than quantitative in character. In the patent, the use of metallic zinc as a dehydrogenating catalyst is specifically mentioned, and the statement is made that when dissociation takes place at 620° to 650° C., a yield of aldehyde corresponding to 80 per cent of the product is obtained. However, when the vapor of isopropanol mixed with air is passed over the heated platinum spiral the reported yield of acetone was only 16 per cent. Secondary butanol yielded but a small amount of methyl ethyl ketone. Secondary octyl alcohol (methyl hexyl carbinol) yielded small amounts of methyl hexyl ketone under the same conditions. Secondary amyl alcohol gave traces of an unidentified ketonic compound. Tertiary butanol was oxidized to acetone and formaldehyde. Since acetone is itself oxidized to formaldehyde in the presence of platinum the formaldehyde might have been obtained either directly or indirectly. Thus,

$$(CH_3)_3COH + O_2 = (CH_3)_2CO + H_2CO + H_2O$$

or by the secondary oxidation of the ketone. Tertiary amyl alcohol behaved in a similar way to yield acetone and formaldehyde. Only negligible amounts of acid were obtained.

Orloff's investigations followed along the same general lines as those of Trillat in that practically the same catalysts were employed but experimentation was conducted on a sufficiently large scale to admit of the possibility of the commercial application of the process. Orloff attempted, however, to correct the faults represented in Trillat's work by placing his investigations on a strictly quantitative basis. With this end in view, he made a careful study (A) of the effect of different temperatures of the catalyst for given concentrations of the air-alcohol mixture and given lengths of catalyst by changing the velocity of flow; (B) of the effect of different concentrations of the gases for constant lengths of catalyst and constant catalyst temperatures by changing the temperature of the liquid alcohol through which the air was drawn in its passage to the catalyst; (C) of the effect of different lengths of catalyst, other conditions being constant. In addition, the rate of flow of gas before entering and after leaving the catalyst was measured as well as the time of contact with the catalyst. The effect of impurities contained in the alcohol was also made the subject of investigation. The study of the comparative efficiency of different catalysts was limited chiefly to the metals, platinum and copper, the latter in the form of gauze or impregnated in finely divided condition in coke or asbestos. As promoters the lower oxides of vanadium, cerium sulfate, thorium oxide and platinum precipitated in finely divided condition on the surface of asbestos were employed. In later experiments, dealing with the oxidation of methanol, external heating of the catalyst was done away with completely by so regulating the percentage of oxygen in the gas mixture as to provide a self-maintained and constant temperature for the reaction. In this case a catalyst consisting of copper filings on asbestos

impregnated with vanadium oxide and supported on copper gauze was used. The initial heating of the entering gases to the temperature required by the reaction was effected by means of a device known as "ignition pills," consisting of pellets of platinized asbestos which were placed in the forward part of the catalytic chamber. This preliminary catalyst promoted sufficient oxidation of the alcohol that the temperature of the gaseous mixture was raised to the reaction point by the heat evolved.

While Trillat and Orloff both emphasized the advantages to be gained by the use of platinum and copper as catalysts in the oxidation of the alcohols, their respective interpretations of the mechanism of the reactions involved in these processes differed very widely. Thus, while the former regarded oxidations in the presence of these metals as reversible reactions, the latter held more strongly to the view that they belong definitely to the class of non-reversible processes. Orloff[13] based his reasoning upon mathematical and thermodynamical interpretations of the oxidation reactions.

Although a great deal of Orloff's work was concerned with the oxidation of methanol, some of the results with higher alcohols are of importance. In general, the oxidation of alcohols higher than methanol required an excess of air to maintain a spontaneous glowing of the catalyst mass. This was explained by the fact that these alcohols have a tendency to dehydrate with formation of water and olefins. This decomposition occurs simultaneously to the oxidation. The hydrocarbon formed by the dehydration is oxidized with the excess of air or oxygen. In the presence of dehydrating catalysts, for example, ethyl alcohol decomposed to give ethylene and this is oxidized intermediately to formaldehyde, or completely to carbon oxides and water.

In the study of the oxidation of the higher alcohols, the concentrations of air and alcohol and the velocity of flow of gas over the catalyst required in each case to maintain the spontaneous glow of the catalyst was experimentally determined. In the oxidation of propyl alcohol the copper catalyst was kept at a dark red heat. Air at the rate of 2.3166 liters per minute carried 1.165 grams of alcohol per liter. The products consisted of aldehyde, equal to about 50 per cent of the alcohol used, hydrocarbons equal to 11.75 per cent, carbon monoxide equal to 1.4 per cent and carbon dioxide equal to 3.6 per cent. The rate of flow was about the same as that required with methanol to maintain the catalyst at glowing temperature.

The catalyst employed in the oxidation of ethanol consisted of 4 rolls of copper gauze 15 cm. long and weighing 40 grams. The temperature of the contact mass was 350° C. at the beginning of the experiment and was maintained at a "cherry red heat" throughout the operation. Air at the rate of 3.89 liters per minute carried 0.7157 grams of alcohol per

[13] Orloff, *Z. physik. Chem.* **69**, 499 (1909); *J. Russ. Phys. Chem. Soc.* **44**, 1596 (1908).

liter. The products of the reaction consisted of acetaldehyde, equal to 66 per cent by weight of the alcohol used, along with small quantities of ethylene, methane, the oxides of carbon and acetic acid. The quantity of air necessary to produce spontaneous glowing of the contact mass was greatly in excess of the theoretical.

The oxidation of isobutyl alcohol was conducted at a temperature of 400° C. at the beginning and at dark red heat throughout the operation. Air at the rate of 3.433 liters per minute carried 1.174 grams of alcohol per liter. The products consisted of aldehyde, equal to a maximum of 52 per cent, carbon monoxide equal to 1.0 per cent, carbon dioxide equal to 3.6 per cent and hydrocarbons equal to 2.4 per cent. The quantity of oxygen was again very largely in excess of that required by theory.

Amyl alcohol (of fermentation) oxidized under exactly the same conditions as isobutyl alcohol gave practically identical yields of aldehyde and gaseous decomposition products. Air at the rate of 3.306 liters per minute carried 1.22 grams of alcohol per liter.

The investigations of Trillat and Orloff directed the attention of chemists to the possibilities presented for the commercial application of vapor phase catalytic oxidations in the field of organic chemistry. The development of the subject from this point on can probably be followed best by considering individually the various adaptations which have been made of particular catalysts to the process. Before proceeding to do this, however, it seems desirable to recapitulate briefly some of the more important features which need to be borne in mind in connection with any catalytic operation on a commercial scale. For practical purposes, oxidation processes may be differentiated into two classes: (a) Those which take place in the presence of dehydrogenating catalysts and which require less than the calculated quantity of free oxygen for the operation. Thus, in the oxidation of methanol to formaldehyde in the presence of finely divided metals, only 40 per cent of the quantity of oxygen calculated on the basis of theory is actually used. (b) Those which take place in the presence of metal oxides, such as vanadium oxide or others of the fifth and sixth groups, and which require for their successful operation as much as four or five times the theoretical quantity of oxygen. The reaction upon which the experiments of Trillat and Orloff were based and which takes place in the presence of such metals as platinum and copper, may be regarded as more or less typical of the first class. This does not represent a simple oxidation process but on analysis is found to consist of a so-called *coupled reaction*.[14] In the first phase, the alcohol decomposes into an aldehyde and hydrogen under the catalytic action of the metal. Such a process is endothermic and therefore requires a constant supply of energy. This energy is generated in the second phase of the reaction by the combination of the hydrogen (which has been liberated in this way) with the oxygen of the air, and is sufficient to make the

[14] LeBlanc and Plaschke, *Z. Elektrochem.* 17, 55 (1911).

process as a whole exothermic in character. In other words, as soon as the initial reaction has taken place, sufficient energy is supplied from within the system to allow the transformation to proceed automatically. The initial reaction may be induced in the case of a copper catalyst by precipitating platinum or palladium black on the metal in the forward part of its length or by some other similar device and after that the quantity of heat generated may be regulated by the velocity of gas flow or by regulating the supply of oxygen. In the case of catalysts other than copper, such as, for example, platinum, nickel and silver, both reactions may be accelerated to such an extent that temperature control becomes difficult. Under these conditions it is frequently convenient to conduct the oxidation in several separate stages, using an insufficient supply of air or oxygen in the first stage and then passing the reaction mixture together with the additional calculated quantity of air over a second and even a third layer of catalyst.

Since catalysts merely affect the rate at which a given reaction approaches equilibrium and not the state of that equilibrium, dehydrogenating catalysts are also active as hydrogenating agents when the conditions are suitable. Thus, platinum, palladium, nickel, cobalt, copper, silver, gold, iron, and aluminum may all act toward either the addition or the splitting off of hydrogen. The formation of aldehydes and ketones by the splitting of hydrogen from an alcohol is favored by temperatures exceeding 200° C. and by diminished pressure, since the reaction is accompanied by increase in volume. The reverse reaction is favored at temperatures in the region of 100° to 150° C. and by pressures higher than atmospheric. For example, ethanol dehydrogenates at 200° to 300° and aldehyde hydrogenates at 150° to 180° C. in the presence of a copper catalyst. In the presence of a nickel catalyst, isopropanol will dehydrogenate to acetone at 250° C. and acetone will hydrogenate to isopropanol at 150° to 180° C. With zinc dust at 300° C. and even under 40 atmospheres pressure, isopropanol dehydrogenates to acetone while with a pressure of 100 to 130 atmospheres the reverse reaction occurs. In discussing catalysts which activate hydrogen at ordinary temperatures and which are therefore of service for hydrogenation-dehydrogenation reactions, Maxted[15] places platinum first. Nickel is not active until at a temperature well above 100° C. but at temperatures between 150° and 350° C. it is a cheap and active catalyst. It cannot be used at temperatures above 400° C. because of sintering and resultant loss of activity. Cobalt is less active than nickel but can be employed at higher temperatures. Iron is even less effective than cobalt at temperatures up to 500° C. but between 500° and 600° C. it is more active than nickel and activates nitrogen as well as hydrogen. Copper is also much less active than nickel toward hydrogen. Since the same metals are also oxygen activating catalysts, they must be regarded as playing a dual rôle in the oxidation of the alcohols. It should also be

[15] Maxted, *J. Soc. Chem. Ind.* **39**, 95T (1920).

noted that members of this group accelerate in varying degrees the decomposition of aldehydes and ketones, viz.,

$$CH_3CHO = CH_4 + CO.$$
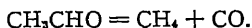
The rate of this decomposition is also accelerated by increases in temperature and in the case of the higher members of the series of alcohols may become so great that the primary products of the oxidation of these substances are decomposed as rapidly as formed.

In any commercial process the following points are important. If the principal reaction is endothermic, the operation will require a continuous supply of heat which may be secured in any of several ways: (a) by preheating one or both of the reacting gases prior to their contact with the catalyst; (b) by electrical or other outside heating of the catalyst; and (c) by internal heat supplied to the system by means of coupled reactions. In cases where the source of heat is to be found in the oxidation of hydrogen to water, the amount of oxygen must be very strictly regulated in order to keep the range of temperatures within favorable limits. To insure this, the percentage of oxygen to inert gas and the velocity of gas flow must be accurately determined from moment to moment and space-time yields must be carefully followed. Mechanical arrangements for securing an intimate mixture of the reacting gases have been devised which are more or less generally based on the countercurrent gas principle. After selection has been made of a given catalyst, attention must be directed constantly to slight variations in its source, its method of preparation, and its exact physical state. After that the arrangement of the catalyst is of extreme importance as shown, for example, in the varied adaptations which have been made of platinum wire in the form of single and multiple gauzes. With metallic catalysts of silver and copper and their alloys, however, the particular shape of the catalyst is relatively unimportant, specially in reaction zones of relatively small cross section. In the case of coupled reactions care must be taken in the combination of two or more catalysts in order to facilitate a selective action which will lead to the formation of the desired product. The walls of the converter or catalyst chamber must be free from substances which tend in any way to induce decompositions in the reacting gases or produce any other than the desired reaction. This chamber may be provided with cooling or heating units, according to the requirements of the particular case.

If the reaction is exothermic, the same general precautions must be observed but in this case provision must be made for cooling the gases before contact with the catalyst or for the external cooling of the catalyst itself. The interchange of heat inside the system may be regulated: (a) by increasing the percentage of inert gas in the reaction mixture; (b) by decreasing the percentage of oxygen and oxidizing in stages, or (c) by operating in a series of short contacts which alternate with coolings of the reaction mixture. In some cases the best results are obtained if

the velocity of gas flow is as rapid as possible and if the gaseous products of the reaction are cooled immediately so as to eliminate as completely as possible pyrogenic decompositions and rearrangements.

It will have been noted that in the experimentation which has been described up to this point the use of platinum and copper as suitable catalysts for promoting the oxidation of alcohols has been emphasized by a large number of investigators. In characterizing the use of platinum in general, it may be said that this metal has been employed for the most part in the form of a finely divided precipitate which is supported on a variety of different carriers such as asbestos, pumice, etc.[16] The porous carrier may be prepared from liquid paste or materials which wholly or partially melt in their water of crystallization. After the addition of platinum chloride the mass is usually dried by blowing a gas through it, which operation may be carried on in the catalytic apparatus itself.[17]

Solid or hollow bodies of non-absorbent, acid-proof and heat-resisting clay molded into balls, cylinders, or plates are also employed.[18] These bodies are covered by a film of absorbent clay to which the platinum salt is applied. Should the outer contact layer become ineffective, the contact substance is dissolved out and a fresh precipitate applied. Or again, the supports or carriers of the contact substance are formed of a material as dense as possible, but possessing sufficient absorptiveness to allow it to be impregnated first with an alkaline solution of platinic chloride. In this way an extremely thin layer of platinum is produced on the support.[19] Again a refractory body such as meerschaum clay or the like is treated with powerful acids (such as aqua regia or sulfuric) for the purpose of removing or preventing the formation of fusible or hygroscopic salts. The material is then washed and mixed (1) with a platinum salt, (2) with an organic compound such as sugar which serves for reducing and also for increasing its porosity and (3) with a volatile acid such as hydrofluosilicic acid or hydrofluoric acid which etches the particles, accelerates the reduction and acts to harden and bind the mass. The mixture produced in this way is molded, dried and freed from all volatile constituents by heating.[20] In cases where unglazed porcelain is used, the material may be broken up into a powder and passed through a sieve having 80 meshes per sq. cm. and then through another having 400 per sq. cm. The mass remaining on the latter is washed, heated with aqua regia, again washed and then calcined. Fifty grams of this "biscuit" powder is heated on a water bath with a solution of 1 gram of platinic chloride in 20 cc. of acidulated water and then dried when excess of concentrated ammonium chloride solution is added. After six hours the clear liquid is decanted, the mass dried on a water bath and then ignited in a platinum crucible. The platinizing process

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[16] Ger. Pat. 134,928 (1901) Majert.
[17] Brit. Pat. 10,412 (1901) Grillo and Schroeder, assrs. to Aktien Gesellschaft für Zink-Industrie. *Compare* Ger. Pat. 128,554 (1901).
[18] Brit. Pat. 618 (1901) Chem. Fabrik vorm. Goldenberg Geromont Co.
[19] Ger. Pat. 188,503 (1906) Neumann.
[20] Brit. Pat. 14,339 (1899) Efrem and Klauder.

is then repeated. It is also of advantage to line the walls of the oxidation chamber with unglazed porcelain which has been similarly platinized.[21] Or the porous supporting material may be treated first with potassium silicate and then with hydrofluosilicic acid or first with barium chloride and then with sulfuric acid. It is then washed and platinized by heating and spraying with a platinum solution which contains a reducing agent, after which it is washed with water or with acids in which the precipitate is insoluble.[22] By this method less platinum is used than by the process described in the German Patent 188,503. Still other catalysts may be prepared by treating a compound of a catalytic metal such as platinic chloride (or solution of salts of copper, zinc and vanadium) with a complex insoluble compound containing one or more easily replaceable bases of the type of artificial zeolite [23] (sodium aluminum silicate). The catalysts may be heated or subjected to reduction before use. A thin film of platinum suitable for oxidation catalysis may also be obtained by coating a perforated hollow metal support.[24] The material for the metallic body constituting the carrier may be of cast iron, copper, zinc, aluminum, etc. Such metallic contact masses are more advantageous than porcelain, asbestos, clay, etc., because of the fact that the contact reaction chamber may be more easily kept at a uniform temperature owing to favorable heat conductivities of these materials.* It may be noted in this connection that traces of grease destroy the catalytic action of platinum,[25] that traces of cobalt [26] and lead [27] act as catalytic poisons and that hydrides of sulfur, tellurium, selenium, phosphorus, arsenic, and antimony inhibit its efficiency.[28]

The action of copper and copper oxides as catalysts seems to depend upon the state and also upon the method of preparation of the substances. Thus, for example, sheet copper or copper in the form of filings has, according to Ipatiew [29] only very slight action upon alcohol vapors at ordinary pressures and at temperatures up to 580° C., while both the metal and its oxide in divided condition readily dehydrogenate ethanol at temperatures below 300° C. with practically no formation of secondary products. The results of experiments by different investigators [30] with what seems to be the same general modification of copper or copper oxide are indeed so divergent that careful attention must be given in every case to the source and also especially to the method of preparation of the particular catalyst which is described in any given experiment. That the

[21] Carrasco and Belloni, *J. pharm. chim.* (6) 27, 469 (1908).
[22] Ger. Pat. 218,725 (1908) Newmann.
[23] Brit. Pat. 8,462 (1914) Badische Anilin u. Soda Fabrik.
[24] Ger. Pat. 225,705 (1908) Niederfuhr.; Chem. Zentr. II, 1107 (1910).
* *Compare* Chapter I.
[25] Faraday, *Ann.* 35, 903 (1888).
[26] Harbeck and Lunge, *Z. anorg. Chem.* 16, 50 (1898).
[27] Maxted, *J. Chem. Soc.* 117, 1280, 1501 (1920); 119, 225 (1921).
[28] Schoenbein, *J. prakt. Chem.* 29, 238 (1843).
[29] Ipatiew, *Ber.* 37, 2961 (1904).
[30] a. Senderens, *Ann. chim. phys.* (8) 13, 266 *et seq.* (1920); b. Taylor, *Trans. Am. Electrochem. Soc.* 36, 154 (1919); c. Zetsche and Zala, *Helv. Chim. Acta* 9, 288-91 (1926); d. Faith and Keyes, *Ind. Eng. Chem.* 23, 1250 (1931).

method of preparation plays an important part in determining the efficiency of copper oxide in one and the same catalytic reaction has been demonstrated by Taylor who has been able to show that if hydrogen is passed over ordinary copper oxide wire of commerce, rapid reduction begins at 300° C., while if the copper so formed is oxidized again at a somewhat lower temperature the copper oxide thus formed will now be reduced by hydrogen below 300° C. By repeating this process copper oxide may finally be obtained which is active toward hydrogen at temperatures as low as 100° C. Copper wire which has been treated in this way is found on examination to present a physical appearance which is similar to that of platinum wire which has been used in ammonia oxidations. Somewhat analogous observations have been recorded by Trillat [31] and Palmer.[32] The former states that fresh red copper is not suitable for use as a catalyst in the oxidation of alcohols and that it is always necessary to ignite it in the oxidizing flame of a bunsen burner so as to coat it with a thin layer of copper oxide. The activity of the copper then continues to increase with use and in the course of time it becomes brittle and disintegrates. The powder which is formed in this way sometimes seems to possess catalytic activity which is almost equivalent to that of platinum sponge. In one case this powder was capable of catalyzing the oxidation of ethanol at a temperature as low as 105° C. It has also been observed that a copper spiral which has been "activated" in this way during the process of oxidizing a given alcohol, loses this acquired condition of "activation" on changing the nature of the alcohol. The behavior of copper as described by Palmer is much the same. This investigator states that the ordinary copper of commerce even when alloyed with zinc [33] has no effect on the oxidation of ethyl and isopropyl alcohols [34] but that copper which has been prepared by the reduction of its oxide readily catalyzes both reactions. In comparing the relative activities of different specimens of copper reduced from its oxide at 215°, 227° and 243° C., respectively, Palmer has observed that the highest efficiency is always displayed by specimens which have been reduced at the lowest temperatures. Copper in the form of gauze seems to possess an efficiency which is comparable to that of a platinum spiral in catalyzing the oxidation of alcohols according to Trillat and Orloff. A comparative and quantitative study of the dehydrogenation of ethyl and amyl alcohols in the presence of copper has been made by Constable,[35] who states that with the catalyst that he employed the rate was found to be the same for both alcohols. At temperatures above 400° C. there are practically no active points which cause dehydrogenation on the surface of copper in the form of either gauze, foil, hammered,

[31] Trillat, *Compt. rend.* **137**, 187 (1903).
[32] Palmer, *Proc. Roy. Soc.* **98A**, 13-26 (1920); **99A**, 412 (1921).
[33] *Compare* Ipatiew, *Ber.* **34**, 3579 (1901).
[34] For the separation of mixtures of water and isopropyl alcohols *see* Labo, *J. Am. Chem. Soc.* **43**, 1005 (1921). For the separation of mixtures of ethyl and isopropyl alcohols *see* Parks and Schwenk, *J. Phys. Chem.* **28**, 720 (1924).
[35] Constable, *Proc. Cambridge Phil. Soc.* **22**, 738 (1925); also *Nature* **116**, 278 (1925); *Proc. Roy. Soc.* **108A**, 355 (1905).

or plated.[36] That a change of surface occurs during the oxidation reaction is shown by the color of a used copper catalyst which may vary from golden yellow to black and is due, probably, to a layer of oxide.

The oxidation of butanol in the presence of a copper catalyst has recently been made the subject of considerable investigation. Weizmann and Garrard [37] state that the yields of butaldehyde are practically theoretical and that about 50 to 100 grams per hour can be obtained from a catalyst mass 45 cm. long and 1.9 cm. in diameter. The method which they employed was that of Bouveault,[38] in which carefully reduced copper hydroxide supported on a copper gauze is heated at a temperature of about 300° C. If care is taken the catalyst does not deteriorate although traces of *n*-butyric acid appear to be formed. If the catalyst is heated at 400° C. further dehydrogenation takes place and crotonaldehyde is formed. This process is subject to patents by Legg,[39] the specifications of which require that normal butyl alcohol be passed in vapor state over a *fused* cupric oxide catalyst or a copper catalyst obtained therefrom. Somewhat more detailed specifications for the catalyst [40] require that cupric oxide or salt of copper which is capable of producing cupric oxide, as for example, cupric carbonate, shall have been raised by heating to the fusion point of copper oxide. This product may then be reduced by hydrogen to give the copper catalyst. The temperature of the catalyst and of the vapors of the reacting gases is maintained at 200° to 350° C. preferably 280° to 320° C. After passing through the catalyst the mixed vapors enter a condenser and are there separated from hydrogen. The mixture of alcohol, aldehyde and acid is then separated by distillation and the unchanged butyl alcohol returned to the catalyzer. A ¾ inch copper tube packed for 26 inches of its length with fused copper oxide and working at 300° C. allows the passage of 240 cc. of alcohol per hour and gives the high conversion of 75 per cent in one passage. The process claims to be adapted to large scale practical working. The transformation of aldehyde to acid is accomplished by adding any oxygen carrying catalyst such as manganese butyrate to the aldehyde and forcing air through the liquid in such a way as to be brought into intimate contact with it at atmospheric or at higher pressures. The operation is accompanied by a rapid rise in temperature at first and this should be so controlled by water cooling as to allow a very gradual rise in temperature to take place up to a point somewhat below the boiling point of the aldehyde (approximately 74° C. or higher, depending upon the percentage of the acid present).

Catalysts of copper oxide mixed with oxides of either molybdenum, vanadium or tungsten caused isopropanol to form 10 per cent, 5.4 per cent, and 11.4 per cent, respectively, of unsaturated hydrocarbons. Under the

[36] Constable, *Proc. Roy. Soc.* 110A, 283 (1926).
[37] Weizmann and Garrard, *J. Chem. Soc.* 117, 328 (1920).
[38] Bouveault, *Bull. soc. chim.* (4) 3, 119 (1908).
[39] Brit. Pat. 173,004 (1921); U. S. Pat: 1,418,448 (1922) Legg, assr. to Adam.
[40] Brit. Pat. 166,249 (1922).

same conditions ethanol gave 0.2, 2.1, and 0.2 per cent and butanol 2.2, 5.4, and 2.0 per cent of unsaturated hydrocarbons, respectively. These catalysts all required external heating to maintain reaction temperature. The tungsten oxide-copper oxide catalyst gave rise also to the formation of formaldehyde in small amounts.[41]

In commercial sized apparatus where the heat lost by radiation or conduction from the reaction chamber is relatively not as great as in the small laboratory tubes, it is necessary to limit the amount of oxidation and also furnish additional material to take up reaction heat as sensible heat. The oxidation of ethanol to aldehyde over a copper catalyst may be controlled by the addition of a volume of steam equal to the volume of alcohol vapor and by the use of only sufficient air to cause the oxidation of half of the hydrogen theoretically liberated by the dehydrogenation of the alcohol.[42] Heat exchange is used to preheat the entering gaseous mixture and to cool the product. Mixtures of hydrocarbons and secondary alcohols such as are obtained in the hydration of the olefins contained in refinery gases are passed with air into heated chambers containing copper catalysts for the oxidation of the alcohols to ketones.[43]

Following the researches of Orloff on the application of copper as a catalyst in the oxidation of the alcohols, the substitution of silver for this metal was given a somewhat marked degree of prominence. Thus, LeBlanc and Plaschke[44] observing the procedure outlined by Orloff but exercising an even more rigorous control of the factors employed, have made a critical study of the behavior of silver in the form of a spiral as a substitute for copper in oxidation reactions. Their results indicate that silver is quite definitely more effective than copper for use in such processes since the maximum yield which Orloff obtained with copper was 55.2 per cent of aldehyde while experiments with a silver spiral 90 mm. long gave a yield of 58 per cent, the highest yield which had been obtained up to this time. The use of the same metal in finely divided condition precipitated upon asbestos has been recommended in a patent issued by Blanck.[45] Somewhat later Fokin[46] in making a comparative study of the relative efficiencies of gold, silver, copper, platinum, cobalt, manganese, aluminum and nickel at high temperatures found that of these the first three are preëminently the best. For example, air saturated with methanol vapor when passed over these various catalysts gave the following yields of formaldehyde, as calculated upon the quantities of methyl alcohol used: Gilded asbestos 71 per cent; silvered asbestos 64 to 66 per cent; copper asbestos 43 to 47 per cent; platinized asbestos 5.2 per cent; reduced cobalt 2.8 per cent; manganese powder 2 per cent; aluminum turnings 1.5 per cent; reduced nickel 1.08 per cent. A mixture of silver and copper gave

[41] Simington and Adkins, *J. Am. Chem. Soc.* **50**, 1455 (1928).
[42] *See* a. U. S. Pat. 1,764,962 (1930) Lacy assr. to Van Schaack Bros. Chem. Works, Inc.; b. Brit. Pat. 325,105 (1930) Woolcock assr. to Imperial Chem. Ind., Inc.
[43] U. S. Pat. 1,541,545 (1925) Wells assr. to Hunt; French Pat. 523,108 (1921) Hunt.
[44] LeBlanc and Plaschke, *Z. Elektrochem.* **17**, 45 (1911).
[45] Blank, Ger. Pat. 228,697 (1910).
[46] Fokin, *J. Russ. Phys. Chem. Soc.* **45**, 286 (1913); *Chem. Abstracts* **7**, 2227 (1913).

the exceptionally high yield of 84 per cent. When silver or gold precipitated in finely divided condition on asbestos is used as a catalyst the initial temperature of the reaction is very low and the heat evolved is sufficient to maintain the reaction at the desired temperature without the application of external heat and without the use of the "ignition pills" which were found necessary by Orloff for starting the reaction in the case of copper.

Moureu and Mignonac [47] following along the lines suggested by Fokin have found that the process of oxidizing with silver or gold precipitated in finely divided condition on asbestos, is capable of very general application, and they have succeeded in obtaining excellent yields of aldehydes in the case of a fairly large number of the higher homologs of methanol. Thus, with silver asbestos, ethanol at a temperature of 340° to 380° C. gave a yield of 89 per cent aldehyde, butanol at 330 to 344° C. gave 93 per cent aldehyde and amyl alcohol (of fermentation) at 320° to 340° C. gave 93 per cent. The silver which was used in these experiments was precipitated on asbestos (cut in squares of 3×5 mm.) from a silver nitrate solution by means of formaldehyde. The catalysis was effected by passing the vapors of alcohol mixed with an insufficient supply of air to oxidize all of the evolved hydrogen into a series of catalytic chambers each consisting of a glass tube 10 to 12 cm. long and loosely filled with the catalytic mass. A thermocouple introduced into the catalyst was used to measure the temperature of the reaction. By suitably regulating the concentration of the entering gases this temperature was most favorably maintained at 230° to 300° C. In passing into the first of this series of chambers the mixture of alcohol and air usually contained about 40 per cent of the total oxygen which was calculated as necessary for complete combustion. On leaving this chamber and before entering the second, an additional quantity of oxygen was added and so on until finally the calculated total amount of oxygen required for the oxidation had been added. In this way, the violence of the oxidation was moderated and local overheating of the catalyst together with the accompanying decompositions was avoided. It is interesting to note that it was frequently found best in practice to employ a little less than the total amount of oxygen calculated on the basis of theory as necessary for the complete oxidation of the material. In the case of the less volatile alcohols the best results were obtained by conducting the operation under diminished (i.e. 20 to 40 mm. of mercury) pressures and at a temperature of 230° to 300° C. Under these conditions yields of 70 to 85 per cent were readily obtained. For example, a twelve-carbon atom alcohol gave an 80 per cent yield of the corresponding aldehyde and geraniol gave citral without decomposition. In some cases pure oxygen may be substituted to advantage for air in the experiment.

[47] Moureu and Mignonac, *Bull. soc. chim.* (4) 29, 88 (1921); *Compt. rend.* 170, 258 (1920); 171, 652 (1920); reviewed in *Chem. Met. Eng.* 22, 1083 (1920).

A comparative study of the efficiency of various metals in the form of turnings or powder which was made at about this time by Senderens [48] also showed that silver headed the list of metal catalysts suitable for the oxidation of alcohols to aldehydes.[49]

Catalysts of 10 per cent copper-90 per cent silver, and silver gauze were found to be most effective with ethanol oxidation; 50 per cent copper-50 per cent silver and 99 per cent silver-1 per cent bismuth were most effective with isopropanol; copper wire and silver gauze were most effective with butanol.[50] Yields of better than 70 per cent of aldehyde or ketone were obtained under the conditions of operation. The catalyst was supported in an externally heated tube half a meter long and seven millimeters inside diameter. The air rate was 83 liters (standard conditions) of air per hour and the alcohol rate very nearly 0.8 mols per hour, a ratio of air to alcohol of very nearly mol per mol. After reaction had begun the heat of reaction was sufficient in most cases to maintain the catalyst at red heat. The conversion in each case may be made more efficient by allowing a smaller conversion of alcohol per pass over the catalyst. With these metal catalysts, three times as much ethanol and twice as much isopropanol break-down to carbon dioxide as butanol. Butanol, however, produced a larger amount of unsaturated hydrocarbons than either of the two other alcohols. The ratio of break-down to carbon dioxide is independent of the kind of metal catalyst and even of the oxide mixtures that remained hot.

Claims have been made to 90 per cent conversions of ethanol to acetaldehyde in the presence of a silver wire catalyst.[51] In this case air was added to the alcohol vapors in sufficient amount to enable the process to be auto-thermal.

The use of nickel as a catalyst has been investigated by Ipatiew, Sabatier, Senderens, Mailhe and many others. According to Mailhe [52] the conversion of alcohols into aldehydes and hydrogen must be regarded as a reversible process in the presence of nickel catalyst,

$$C_2H_5OH \;\rightleftharpoons\; CH_3CHO + H_2$$
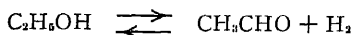
temperatures of 150° to 180° C. favoring alcohol formation and temperatures of about 250° C. favoring aldehyde formation. Specifications for the preparation of a nickel catalyst are as follows: An inert absorptive and relatively bulky material such as infusorial earth (silica) is impregnated with a solution of a reducible nickel salt containing oxygen, and then dried, finely divided and reduced with hydrogen. Or the nickel may be precipitated as an insoluble salt and soluble salts removed by washing prior to the drying and reduction of the powder.[53]

[48] Senderens, *Ann. chim. phys.* **13**, 266-83 (1920).
[49] *See also* Brit. Pat. 290,523 (1929) Goldschmidt, which claims a silver catalyst at 400° to 420° C. for ethanol oxidation.
[50] Simington and Adkins, *J. Am. Chem. Soc.* **50**, 1449-56 (1928).
[51] Ger. Pat. 422,729 (1926) Holzverkohlungsind.
[52] Mailhe, *Chem. Zentr.* 1921, I, 717.
[53] U. S. Pat. 1,004,034 (1911) Procter and Gamble Co.

The statement has already been made that when butanol was oxidized in the presence of a copper catalyst at 400° C., crotonic aldehyde was formed. In this connection it is interesting to note that a patent has been issued [54] in which a process for the catalytic manufacture of butyric aldehyde and butyl alcohol from crotonic aldehyde by hydrogenation in the presence of water or steam is claimed. The operation may be carried out at ordinary pressures or at higher than atmospheric pressures. In the former case the reaction tube is charged with a nickel catalyst prepared by precipitation on pumice, kieselguhr or the like, in the proportion of 5 to 15 parts of metallic nickel to 100 parts of the inert material. The tube is heated at 110° to 120° C. and crotonic aldehyde mixed with 20 to 25 per cent water is swept through it by means of a stream of hydrogen. Fatty acids of the palmitic acid series may be prepared by oxidizing butanol and then subjecting the product to simultaneous hydrogenation and polymerization.[55] An apparatus is described in general terms. Mixtures of fatty acids (formic, acetic, etc., up to C_8) along with the corresponding alcohols and aldehydes have also been obtained by passing a mixture of carbon monoxide and hydrogen in which the hydrogen compressed at 150 atmospheres is in excess, through an electrically heated high pressure apparatus at 450° to 500° C. The contact consists of iron in the form of cut shavings mixed with potassium carbonate. The latter must be regarded as not merely serving to activate the metal but as playing an important rôle and must be supplied in definite and fairly large quantities.[56]

A most satisfactory comparison of the activities of supported and unsupported catalysts of silver, copper, and nickel may be obtained from the results of experiments made by Faith and Keyes,[30d] who worked with methanol and ethanol. The fact that uniform methods of catalyst preparation, support, and size, and uniform methods of operations were used adds much to the value of the results. In all cases the catalyst mass was 45 mm. long by 12 mm. in diameter, the alcohol saturator was maintained at 45° C. for ethanol and at 36° C. for methanol, and the temperature of the hottest point in the catalyst mass was determined with a thermocouple embedded in the mass. In the case of ethanol oxidation the highest conversions to acetaldehyde per pass were obtained under the following conditions: (1) silver gauze catalyst; flow rate 0.57 liters per minute; catalyst temperature 515° C., 80.6 per cent conversion to aldehyde; 13.3 per cent conversion to carbon dioxide; and 3.2 per cent conversion to acid, (2) silver oxide supported on asbestos; flow rate 0.37 liters per minute; catalyst temperature 595° C.; (conversions as above) 72.3 per cent; 14.5 per cent; 2.9 per cent, (3) copper turnings catalyst; flow rate 0.62 liters per minute; catalyst temperature 512° C.; (conversions) 78.0

[54] Brit. Pat. 147,118 (1920) Grünstein.
[55] Brit. Pat. 156,755 (1922) Soc. Française des Destilleries de l'Indo-Chine (1920).
[56] Fischer and Tropsch, *Ber.* 56, 2428 (1923); *Brennstoff Chem.* 5, 201, 211 (1924) *Abhandl. Kohle* 5, 230 (1920); 6, 330, 366 (1921).

per cent; 14.1 per cent; 2.8 per cent, (4) copper oxide on asbestos; flow rate 0.3 liters per minute; catalyst temperature 498° C.; (conversions) 73.0 per cent; 12.6 per cent; 2.6 per cent, (5) nickel gauze catalyst; flow rate 0.45 liters per minute; catalyst temperature 560° C.; (conversions) 29.6 per cent; 18.9 per cent; 0.5 per cent, (6) nickel oxide on asbestos; flow rate 0.31 liters per minute; catalyst temperature 540° C.; (conversions) 10.9 per cent; 14.0 per cent; trace. In the case of methanol oxidation the highest conversions to formaldehyde per pass were obtained under the following conditions: catalysts same as above in ethanol oxidation; conditions and conversions in the same order as before: (1) 0.89; 460° C.; formaldehyde 60.0 per cent; carbon dioxide 27.3 per cent; carbon monoxide, none, (2) 0.43; 475° C.; 56.7 per cent; 22.3 per cent; carbon monoxide none, (3) 0.62; 420° C.; 45.7 per cent; 19.5 per cent; carbon monoxide none, (4) 0.72; 43.6 per cent; 31.5 per cent; carbon monoxide none, (5) 0.72; 600° C.; 15.6 per cent; 14.6 per cent; carbon monoxide 59.6 per cent, (6) 0.68; 550° C.; 1.6 per cent; 32.8 per cent; carbon monoxide 36.0 per cent. The results of the work serve to show that the form of a catalyst having the greatest coefficient of heat transfer, i.e. metallic catalyst not supported on an inert carrier, gives the highest conversion of alcohol to aldehyde in vapor phase oxidations. The conversions with silver and copper catalysts compare favorably with the highest reported elsewhere in the literature. Nickel is a poor catalyst in the case of methanol because it causes considerable decomposition to carbon monoxide and in the case of ethanol because it gives only low rates.

Although metallic zinc catalysts activated dehydrogenation of the alcohols, they do not act as active catalysts for the oxidation of the evolved hydrogen. This is also true where high zinc brasses are used as catalysts.[56] As the amount of hydrogen present in the evolved mixture is larger in the case of ethanol than in the case of butanol or isopropanol, the more ready dehydrogenation of ethanol over this catalyst is indicated. With zinc catalysts 40 to 70 per cent yields of aldehydes are obtainable at 580° C. from amyl or isobutyl alcohols.[57] Under these conditions from 10 to 15 per cent of alcohol is destroyed completely. Brass has been recommended as a catalyst for the oxidation of secondary alcohols to ketones by air and in the presence of steam.[58] Temperatures ranging from 500° to 800° C. are mentioned. Although the oxidation of isopropanol to acetone may be conducted at 200° C. in the presence of brass gauze with a 90 per cent yield, the reaction is essentially one of dehydrogenation.[59] The virtue of the oxygen in the process lies in the supplying of heat to make the process independent of external heating since acetone may be obtained without the use of oxygen if external heat is supplied the reaction.

[57] Danilov, *Trans. State Inst. App. Chem. (Moscow)* 1927, No. 5, 66-88; *Chem. Abstracts* 22, 2138 (1928).
[58] U. S. Pat. 1,460,876 (1923) Williams and White; U. S. Pat. 1,497,817 (1924) Wells.
[59] Footnote, Sabatier and Reid, "Catalysis in Organic Chemistry," New York, D. Van Nostrand Co., Inc., 1923, p. 256.

Simultaneously with these developments in the use of various metal catalysts in oxidation processes, attention was given to the behavior of different oxides of the metals, metalloids and non-metals. In the case of the metal oxides, catalytic action is much the same as that observed for the corresponding metals due to the fact that they are first reduced by the vapors of the oxidizing substance to the metals or their lower oxides and these are then re-oxidized to form the higher oxides in the presence of the oxygen of the air, the process being a continuous one. This is particularly true of the iron, manganese, nickel, cobalt, and copper and in the case of the latter can be followed by means of color changes which may be observed to take place successively in the catalytic mass. With copper oxide the reaction takes place between 180° and 260° C.[60] In the case of the above metals catalytic action is always accompanied by the reduction of the metal and Senderens [61] is inclined to the opinion that the metals themselves in finely divided condition are to be preferred as catalysts to their corresponding oxides. Ipatiew,[62] on the other hand, points out that whereas copper and tin do not decompose alcohol to aldehyde, cupric oxide and tin oxide do and that the reaction is always accompanied by the reduction of the metal. A patent [63] describes the use of one or more oxides of manganese, iron, bismuth, cobalt, copper, lead and silver. These oxides are prepared by precipitation in as finely divided condition as possible and carefully freed from water, including water of hydration at temperatures not to exceed 250° C. The catalyst may be used as a porous agglomerate or broken into porous granules. In order that oxidation of alcohols, aldehydes and other substances may take place at ordinary temperatures, it is necessary that all traces of moisture should be removed from them and that the gases should be perfectly dry. In order to produce metallic oxides in an extremely finely divided and voluminous condition [64] a concentrated aqueous solution of its nitrate is mixed with an organic compound, preferably one that is soluble in water and rich in carbon and which is subsequently decomposed by heat. On heating, the evolution of gas causes the oxide to swell up to large volume and at the same time the whole of the carbon present in the organic compound is removed by combustion. On reduction at temperatures of 200° to 300° C. these oxides may be transformed into the corresponding voluminous and catalytically active metals.

The metal oxides thus far considered belong, in general, to the class of those which are reducible at moderately high temperatures in the presence of water or of alcohol. To the class of the so-called irreducible oxides of the metals and non-metals belong those of zinc, aluminum, molybdenum, silicon, and vanadium and chromium sesquioxide. The last has been described by Sabatier and Mailhe [65] as affording an excellent

[60] Woog, *Compt. rend.* 145, 124 (1907).
[61] Senderens, *Ann. chim. phys.* (8) 25, 449 (1912).
[62] Ipatiew, *Ber.* 40, 128 (1907).
[63] Brit. Pat. 166,285 (1920) Scalione and Frazer.
[64] U. S. Pat. 1,200,696 (1916) Bedford and Erdmann.
[65] Sabatier and Mailhe, *Compt. rend.* 142, 1394 (1906).

oxidation catalyst and its application for use in the oxidation of alcohol at dull red heat has been patented.[66] Of the others, zinc oxide and vanadium pentoxide have been recommended by Senderens [67] as superior to any of this general class. A zinc oxide catalyst prepared by impregnating pumice with $(NH_4)_2ZnO_2$ and heating to drive off water and ammonia, when used at 315° to 350° C. gave yields varying from 60 to 93 per cent of aldehydes and ketones from normal and isopropanols, normal, secondary, and isobutanols, isoamyl alcohol and 2-octanol.[68] In 1909 Sabatier and Mailhe [69] recommended the use of the oxides of silicon and molybdenum for use in the oxidation of the alcohols and in 1913 Senderens [70] made a quantitative study of the behavior of these and other oxides of this class including vanadium pentoxide in the presence of air. The latter investigation is of interest from the point of view of the classification of the catalysts in the ratio of their relative activity but does not allow of a precise estimate of the value of a particular catalyst in a given operation since the percentage of air and alcohol in the gaseous mixtures is not defined. This is to be regretted particularly because the nature or course of the reaction in such cases is largely determined by the concentration of the air-alcohol mixture.

The activity of vanadium pentoxide has been especially emphasized as a result of the investigations of Neumann, Moeser and Lindenbaum,[71] who describe its effect upon a mixture of ethyl alcohol and air as being very similar to that of finely divided platinum. The oxide which was used in these experiments was precipitated in finely divided condition upon asbestos. When the air was passed through ethanol maintained at 55° C., and the mixture of air and vapor passed over a gently heated vanadium pentoxide-asbestos catalyst, the catalyst starts to glow and continues to do so without further external heating.[50] Both aldehyde and acid are formed. Preparations of vanadium oxide as a catalyst for alcohol oxidations have been patented,[72] still others will be referred to later in the text and a fairly extensive bibliography of vanadium compounds is available.[73]

Various processes describing the application of the oxides of elements of the fifth and sixth groups have been reported in the literature. Since, however, most of these compounds have been recognized as dehydrating catalysts, the consideration of their various uses will be deferred for consideration in a later chapter in connection with the oxidation of hydrocarbons. It may be stated at this point, however, that the use of silica and alumina in conjunction with various metallic oxides, and particularly

[66] Brit. Pat. 1,181 (1871) Aubertin.
[67] Senderens, *Compt. rend.* **156,** 1909 (1913).
[68] Ottensooser, *Bull. soc. chim.* **41,** 324-5 (1927).
[69] Sabatier and Mailhe, *Bull. soc. chim.* (4) **5,** 132 (1909).
[70] Senderens, *Bull. soc. chim.* (4) **13,** 628 (1913); *Ann. chim. phys.* (9) **13,** 266-83 (1920).
[71] Neumann, Moeser and Lindenbaum, *J. prakt. chem.* **75,** 46 (1907).
[72] a. U. S. Pat. 1,318,631-2-3 (1919) Weiss and Downs, assrs. to The Barrett Co.; b. Brit. Pat. 2,745 (1871) Pinkney; Brit. Pat. 238,033 (1924) Maxted and Coke; c. Brit. Pat. 8,462 (1914) Badische Anilin u. Soda Fabrik; d. U. S. Pat. 1,636,952 (1927) Craver.
[73] a. "Die Literature des Vanadin," (1804-1905) Prandtl, Hamburg, Verlag v. Voss; b. Alexander, *J. Soc. Chem. Ind.* **48,** 899 (1929).

copper, has proved very valuable in catalytic oxidations.[74] The efficiency of pumice for such purposes was recognized very early in the history of the study of these processes and has recently been made the subject of renewed investigations. For example, a catalyst [75] has been recommended which consists of finely powdered silica and cupric oxide mixed with granular alumina, the mixture having been heated to a temperature above the melting point of the copper compound. Under these conditions the silica reacts with a portion of the copper oxide and the remainder coats the particles of alumina thus forming a porous contact mass the surface of which is covered with a film of copper oxide. A similar catalyst [76] consists of a mixture of copper and copper oxide mixed with clay or other substances which contain silicates to which alumina has been added. The presence of alumina prevents the copper and copper oxide particles from fusing with the silica in the form of silicates at the high temperatures necessary for the oxidation processes, thus rendering the porosity of the mass perfect and at the same time allowing for the distribution of the copper in the form of a fine film. Other metals and metallic oxides have been recommended for use in conjunction with alumina.[77] For example, the "fibrous alumina" or sprouted alumina of Wislicenus (obtained by strongly igniting aluminum sulfate, nitrate or acetate or by the oxidation of aluminum powder in the presence of water and a trace of mercury) has the power to remove from their solutions by absorption many metals and metallic oxides. The chlorides, nitrates or acetates of the metal are treated respectively with ammonia until the precipitate which is first formed is redissolved when the "fibrous alumina" is added. The mass is then washed, dried and ignited. The "metallic oxide aluminas" produced in this way have characteristic colors which vary with the concentration of the metallic salt that was used in their preparation. These aluminas are capable of effecting many types of catalytic oxidation and are in particular applicable to the catalysis of alcohol-air mixtures. Still another catalyst [78] which has been recommended and falls into this same general class, contains a mixture of 85 per cent hydraulic cement, 10 per cent copper oxide and 5 per cent alumina. This is effective for oxidations at temperatures of 210° to 220° C. but is most efficient at about 360° C. In the case of contact masses which consist of a clay or brick base the corresponding temperatures are 650° to 700° and 780° to 825° C.

Activated charcoal, obtained from peat, lignite, anthracite coal, etc., has also been mentioned as a catalyst for the oxidation of alcohols to aldehydes and acids.[79]

Comparison of the oxidation of aliphatic alcohols in the vapor phase by air without catalysts and with metallic catalysts of magnesium, alumi-

[74] Marchand, *Ber.* 13, 987 (1882).
[75] U. S. Pat. 1.007.516 (1911) Beckman, assr. to American Cynamid Co.
[76] a. U. S. Pat. 1 007,516 (1911) Beckman to American Cyanamid Co.; b. Fr. Pat. 453,079 (1913) Nitrogen-Gesellschaft.
[77] Kleinstuck, *Z. angew. Chem.* 32, 1105 (1910).
[78] Ger. Pat. 312,726 (1912) Nitrogen Gesellschaft.
[79] Ger. Pat. 203,848 (1907) Dennstedt and Hassler; *Chem. Ztr.* 1908, II, p. 1750.

num, and zinc, and with metallic oxide catalysts of molybdenum, tungsten, thorium, and silica shows that these catalysts are practically indifferent toward the reaction.[67] With dry air and no catalyst oxidation begins at 380° to 405° C. and at 410° to 450° C. the oxygen is taken up completely.

Certain of the rare earth oxides are very active catalysts. The introduction of small amounts of samarium oxide to a copper oxide catalyst enabled lower temperatures to be used in the oxidation of ethanol although it also reduced the yields of aldehyde obtainable probably because of the catalytic effect of the rare earth oxide on the decomposition of aldehyde.[80] Thus, with 482° C. as the best temperature under the conditions with a copper oxide catalyst, the introduction of 0.5, 1.0, 2.0, and 5.0 per cent amounts of samarium oxide lowered the effective temperatures to 460°, 465°, 395°, and 370° C., respectively. Considerable excess of oxygen was used in these experiments, 0.40 to 0.43 liters of oxygen per gram of ethanol as compared to 0.2434 liters theoretically necessary, and probably accounts for a part of the alcohol destruction. However, considerable charring was evident with these catalysts unless an excess of air was present. It is apparent that such active catalysts are of no utility in the oxidation of such readily oxidized substances as the alcohols.

The direct oxidation of alcohol to acetic acid in one step would be a highly desirable method of operation, but the difficulties of insuring complete oxidation of the intermediately formed aldehyde without at the same time causing complete oxidation to carbon dioxide have largely prevented the development of any ordinary process employing oxygen directly as the oxidizing agent. Methods have been tried, at least experimentally,[50, 81a] with the object of operating the alcohol oxidation and the aldehyde oxidation processes directly connected in series. But the yields have been low and the maintenance of proper operating conditions very sensitive.

A process has been proposed,[81b] however, in which air is used indirectly and the coupled reaction, consisting of dehydrogenation of the alcohol followed by oxidation of the aldehyde, accomplished in the presence of a single metal catalyst in different stages of oxidation. A catalyst composed of copper oxide containing about one per cent of silver oxide as a promoter moves counter currently in a tower to an entering stream of vaporized alcohol and water. The alcohol-water vapors entering the lower part of the tower, which is at a temperature of about 280° C., meet the metallic catalyst, which has been reduced in the upper portion of the tower, and is dehydrogenated to aldehyde and hydrogen. The aldehyde and hydrogen passing up the tower are oxidized by the copper oxide, which is itself reduced to the metal. The upper portion of the tower is maintained at a temperature of about 350° C. With commercial alcohol of 80 per cent strength, yields of 94 per cent of glacial acetic acid are claimed. The process is open to the obvious objection that solids must be circulated. It

[80] Lowdermilk and Day. *J. Am. Chem. Soc.* **52**, 3535 (1930).
[81a] Makoverkii and Yanooskii. Russ. Pat. 1,420 (1926).
[81b] Brit. Pat. 287,064 (1927) Hale and Haldeman.

is necessary to remove metallic copper at the bottom of the tower, oxidize this in a separate operation and introduce the fresh oxide in the top of the tower. The advantages of the spontaneous generation of heat in the direct oxidation process is also lost especially in the dehydrogenation portion of the tower which must depend upon the heat content of the descending copper catalyst for maintaining temperature if external heating is to be avoided, since the dehydrogenation reaction absorbs heat. Heat interchange between hot products and cold reactants would eliminate the necessity for supplying sensible heat to the water-alcohol vapors at the expense of the catalytic mass in the lower part of the tower.

The presence of water vapor with the alcohol vapor not only helps in controlling the reaction but is essential thereto since dry metallic oxides, or silver oxide, will not react with anhydrous acetaldehyde.[82] Dry formaldehyde, on the other hand, reduces silver oxide with the formation of carbon monoxide.

A number of other processes have been patented for the direct oxidation of ethanol to acetic acid. One of the earliest of these was described by Walter,[83] who passed mixtures of ethanol, air, and steam over different catalysts. Since this early disclosure many catalysts have been patented for use at various temperatures. Thus, carbon in the form of coke, etc.,[84] is claimed to be effective with air-ethanol mixtures at 150° to 300° C., copper compounds at 270° C.,[85] metallic vanadates at 250° to 300° C.,[86] and silver catalysts at temperatures 380° to 440° C.,[87] to low red heat. Hunt claims the formation of acids from a mixture of isopropanol, olefins, air, and steam in the presence of copper compounds at 200° C.[88]

Reaction of Carbon Monoxide with Alcohols to Form Acids

The reaction of carbon monoxide with alcohols to form fatty acids, having one more carbon atom per molecule than the alcohol, has recently received attention. The experimental work with the reaction has been based largely on one of the proposed mechanisms for the formation of higher alcohols from mixtures of hydrogen and carbon monoxide.[89] Thus, the mechanism first proposed occurred through the following steps:

$$H_2 + CO \qquad = H_2CO \text{ (formaldehyde)}$$
$$H_2CO + H_2 \qquad = H_3COH \text{ (methanol)}$$
$$H_3COH + CO \qquad = H_3C.CO.OH \text{ (acetic acid)}$$
$$H_3C.CO.OH + 2H_2 = H_3C.H_2C.OH \text{ (ethanol)} + H_2O$$
$$\text{etc.}$$
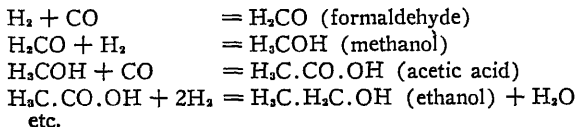
[82] Wieland, *Ber.* 45, 2606-15 (1912).
[83] Ger. Pat. 168,291 (1904); Brit. Pat. 21.941 (1905); French Pat. 360,785 (1905) Walter.
[84] Ger. Pat. 203,848 (1907) Dennstedt and Hassler.
[85] French Pat. 526,567 (1920) Mailhe.
[86] Brit. Pat. 238,033 (1924) Maxted and Coke.
[87] a. U. S. Pat. 1,666,447 (1928); Brit. Pat. 290,523 (1927) Goldschmidt; b. Brit. Pat. 294,037 (1927) Holzverkohlungsind.
[88] U. S. Pat. 1,541,545 (1925) Hunt.
[89] Brit. Pat. 20,488 (1913) Fischer assr. to Badische Anilin u. Soda Fabrik.

However, this proposed mechanism has not found experimental substantiation and has in fact been quite largely disproved.[90] Hence, it is somewhat difficult to establish the industrial utility of the proposed organic acid synthesis on the basis of the higher alcohol mechanism.

The mechanism generally accepted at the present for higher alcohol synthesis is by the direct condensation of the lower alcohols through the elimination of water. Thus,

$$2CH_3OH = C_2H_5OH + H_2O.$$

Acids, which may be present in the reaction mixture in the form of esters and not as free acid, are formed, according to the evidence that has been presented, by the polymerization of aldehydes followed by molecular rearrangement,

$$2CH_3CHO = CH_3CO.OC_2H_5,$$

rather than by the intermediate formation by addition of carbon monoxide to an alcohol,

$$CH_3OH + CO = CH_3CO.OH.$$
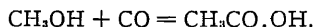
Indeed, the use of excess carbon monoxide in the presence of alcohols favors the condensation to higher alcohols by removing the water, which forms, by the reaction,

$$H_2O + CO = CO_2 + H_2.$$
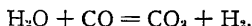
Even on the basis of the published results of the catalytic and non-catalytic decomposition of acetic acid, no such reaction may be predicted. Ordinarily, the mechanism of decomposition of an organic oxygenated molecule is considered to be of aid in interpreting possible mechanisms for synthesis.[91] It is of aid in predicting possible side reactions that might occur during the synthesis. This is of value, particularly if the decomposition products are other than the reactants, since it shows the necessity for stabilizing the synthesized molecule.

With the exception of formic acid, the lower fatty acids are quite stable up to relatively high temperatures. Cahours and Berthelot early noted[92] the thermal stability of these acids, and the latter reported that acetic acid did not decompose until above a dull red heat. More recently Senderens showed that acetic, propionic, *n*-butyric, isobutyric, and isovaleric acids were perfectly stable at temperatures as high as 460° C.[93] At higher temperatures these acids undergo pyrogenic decomposition to yield simple and stable substances. In the case of acetic acid, Nef[94] reported the presence of methane, carbon dioxide, carbon monoxide, ethylene, hydrogen, and acetone in the products from decomposition.

[90] a. Cryder, Thesis for D.Sc. (1930), Massachusetts Institute of Technology, Cambridge, Mass.; b. Frolich and Cryder, *Ind. Eng. Chem.* 22, 1051-7 (1930).
[91] Matignon, *Bull. soc. chim.* 37, 825-36 (1925); *also* Chapter I.
[92] a. Cahours, *Compt. rend.* 19, 771 (1844); b. Berthelot, *Ann. chim. phys.* III, 33, 295 (1851); 53, 187 (1858).
[93] Senderens and Aboulenc, *Compt. rend.* 170, 1064 (1920).
[94] Nef, *Ann.* 318, 221 (1901).

In the presence of catalysts, the decomposition of acetic acid can be made to occur primarily by either demethanization, deketonization, or dehydration. Catalysts such as nickel, sodium hydroxide, sodium carbonate, and animal charcoal promote demethanization. The deketonizing catalysts include: finely divided cadmium, iron, aluminum, lead, and copper; the oxides of thorium, uranium, iron, chromium, calcium, titanium, tin, zinc, and manganese; the carbonates of barium, strontium, calcium, and zinc; the chlorides of sodium, barium, and calcium; zinc dust; copper-aluminum alloy; and ferrosilicon. Catalysts which have been found to promote dehydration comprise: chlorides and sulfates of alkali and alkaline earth metals; phosphoric, boric, tungstic, hydrochloric, hydrobromic, and hydriodic acids; the sodium salts of phosphoric, tungstic or boric acids; sulfur dioxide; sulfur oxychloride; non-crystalline carbon; many organic substances such as organic bases, phenol and its derivatives, polyhydric alcohols, and some of the aliphatic acid derivatives. Catalysts which promote the splitting out of a ketone may also function toward dehydration.

The formation of methanol in the catalytic decomposition of acetic acid has not been reported. This is somewhat to be expected since it is probable that methanol would be unstable at the temperatures required for the acetic acid decomposition. However, catalysts which direct the decomposition to hydrogen and carbon monoxide have not been reported, and no basis is to be had regarding the efficacy of the numerous substances that have been patented for the synthesis.

It may be concluded that although the reaction is thermodynamically possible, and although considerable effort has apparently already been expended in a search for catalysts, the side reactions are so numerous and involved in the addition of carbon monoxide to alcohols to form fatty acids that the industrial phase has not yet been reached. It should not be concluded, however, that the difficulties cannot be overcome.

Thermodynamically, the addition of carbon monoxide to methanol to form acetic acid is favorable at low and moderate temperatures but less so at temperatures higher than about 450° to 500° C. For the reaction,

$$CH_3OH + CO = CH_3COOH,$$
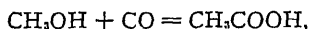
the free energy change as a function of temperature may be represented [nn] by the equation:

$$\Delta F = -27540 + 11.5T \log T + 0.0019T^2 + 1.0T.$$

From this equation: $\Delta F = -11300$ at 225° C.; -8200 at 300° C.; -4150 at 400° C.; and becomes equal to 0 at 500° C. Notwithstanding this unfavorable temperature effect, favorable conversions should be possible at these higher temperatures by the use of pressure since the reaction occurs with a decrease in volume. Vapor phase processes that have been proposed take into consideration this effect of pressure and are usually specified to operate under several hundred atmospheres pressure.

In liquid phase processes it has been possible to add carbon monoxide to alcohol through the sodium salt of the alcohol. Thus, Genther [95] early showed that carbon monoxide would react with sodium ethoxide at 190° C. to form sodium propionate. It should be noted that in reactions

$$C_2H_5ONa + CO = C_2H_5.CO.ONa$$

<div style="text-align:center">sodium ethoxide   sodium propionate</div>
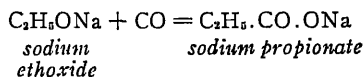
of this nature the sodium does not act in the capacity of a catalyst but in the capacity of a reagent since reaction ceases as soon as the sodium alcoholate has been reacted.

It has been claimed, however, that when carbon monoxide is reacted with aliphatic alcohols in the liquid phase and in the presence of dissolved alkali metal alcoholates, the corresponding alkyl formates are readily formed.[96] For example, ethanol containing 1.5 per cent

$$ROH + CO = R.O.OCH$$
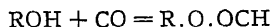
dissolved sodium metal is subjected to a pressure of 150 atmospheres of carbon monoxide at 70° C. for four hours. About 90 per cent conversion to ethyl formate is obtained. Brass, silver or Krupp V2A steel is used for lining the reaction vessel to prevent formation of metallic carbonyls which tend to cause secondary reactions giving a colored and impure product. If such a conversion is possible, then it is obvious that in this case the alkali metal acts as a catalyst.

In the proposed vapor phase processes for organic acid synthesis, carbon monoxide is passed with the vaporized aliphatic alcohol over catalysts similar in nature to those employed in the pressure synthesis of higher alcohols from hydrogen-carbon monoxide mixtures. Pressures on the order of 200 atmospheres are employed. Temperatures of about 200° to 300° C. are preferred but it is necessary to use somewhat higher ones in order to obtain sufficient reaction. Mixtures of the oxides of zinc and chromium or copper, promoted with alkali or alkaline earth oxides, are suitable catalysts for the formation of carbon-carbon linkages.[97] Catalysts composed of an alkali, chromium, and molybdenum have been claimed for the synthesis of mixtures of higher alcohols, aldehydes, acids, esters, etc., from carbon monoxide and vaporized aliphatic alcohols as methanol, ethanol, etc., at temperatures of about 420° C. and a pressure of 200 atmospheres.[98]

For producing acetic acid, carbon monoxide and methanol may be passed over catalysts composed of the oxides of copper, tin, lead, zinc, or acetates of copper, zinc, or methylates of zinc, aluminum, tin, etc. These catalysts or mixtures of them are preferably promoted by the use of more

[95] Genther, *Ann. C.* 402, 290 (1880).
[96] Brit. Pat. 252,848 (1925) Badische Anilin u. Soda Fabrik.
[97] U. S. Pat. 1,562,480 (1925) Badische Anilin u. Soda Fabrik.
[98] Wietzel and Wietzel, U. S. Pat. 1,562,480 (1929).

basic materials such as the acetates or methylates of potassium or sodium.[99a] In operation carbon monoxide at 80 to 120 atmospheres is bubbled through liquid methanol maintained at a temperature of 60° to 70° C. and then through a chamber filled with the catalyst maintained at a temperature of 250° to 300° C. By this method the operation is conducted in the presence of a considerable excess of carbon monoxide. Since no operating data are available, the process cannot be evaluated.

There is some question as to whether acetic acid would be formed from the reaction in the presence of the more alkaline catalysts, since it has been claimed that by passing a mixture of carbon monoxide and methanol vapor over solid sodium methoxide under high pressure, methyl formate is formed: [99b]

$$CH_3OH + CO = HCO.O.CH_3.$$
$$\text{\textit{methanol}} \qquad \text{\textit{methyl formate}}$$
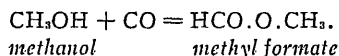
In studies of the decomposition of methanol alone in the presence of such catalysts as zinc oxide-copper oxide or zinc oxide-chromium oxide methyl formate has been noted in the decomposition products showing that there is some tendency to form this substance even at atmospheric pressure.

Catalysts having a very acid nature such as metaphosphoric acid, arsenious acid, boric acid, or salts of these acids have been proposed. The addition of copper as such or as the formate serves to promote the reaction.[100] Reaction chambers extremely resistant to corrosion must be used. Catalysts such as zinc arsenite, or zinc or chromium metaphosphate having a highly acidic nature are claimed to be effective in the formation of organic acids from carbon monoxide and alcohols at temperatures of about 300° C. and a pressure of 200 atmospheres. Even with such acidic catalysts considerable quantities of esters are stated to be formed.[101]

In general, carbonyl forming metals such as nickel, iron or cobalt, must not be present in the formation of metallic carbonyls as their presence in one part of the apparatus may lead to the subsequent deposition of the metal on the catalyst by the decomposition of the carbonyl in a hotter portion of the apparatus, with destruction of the catalyst activity. The catalysts may be activated by the addition of metal halides such as potassium fluoride or iodide, sodium chloride, or aluminum chloride.[102]

In all cases considerable excess of carbon monoxide has been proposed for the reactions. This not only forces the reaction to go to completion but also prevents undue polymerization and condensation of the alcohol

[99a] Dreyfus, Brit. Pats. 264,558 (1925); 268,845 (1925); U. S. Pats. 1,697,109 (1929); 1,743,659 (1930); 1,784,583 (1930).
[99b] U. S. Pat. 1,302,011 (1919) Christiansen.
[100] a. Brit. Pats. 283,989 (process); 317,867 (catalyst) (1928) British Celanese Ltd.; b. Brit. Pat. 320,457 (1928) I. G. Farbenind; c. French Pat. 35,963 (1928) addn. to 597,328 Badische Anilin u. Soda Fabrik; d. French Pat. 637,763 (1927) Dreyfus; e. Brit. Pat. 337,053 (1929) Bader assr. to British Celanese; f. Brit. Pat. 338,329 (1929) Soc. Fr. de Cat. Gen.
[101] Swiss Pat. 137,737 (1929) I. G. Farbenind; *Zentr.* II, 465 (1930).
[102] Brit. Pats. 240,955 (1926); 254,819 (1926); 320,457 (1928); 323,475 (1928); 323,513 (1928) I. G. Farbenind.

or products such as would occur were high concentrations and partial pressures of alcohol used.

Alkyl halides have been claimed to react with carbon monoxide to form the corresponding acid halides. Thus:

$$RHal + CO = R.CO.Hal.$$
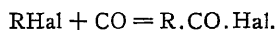
As catalysts for this reaction, inorganic acids having low volatility and high stability at the temperatures necessary may be used. Phosphoric acid or phosphates, boric acid, boric anhydride or borates may be used either in the molten state, supported on inert carriers, or as the solid salts.[103] The use of excess amounts of carbon monoxide and high pressure are specified. Thus, when one volume of methyl chloride and 8 volumes of carbon monoxide are passed, as a mixture, over sodium metaphosphate on pumice at 700° to 800° C. a conversion to 10 or 15 per cent of acetyl chloride is obtained. The use of pressure enables much higher yields to be obtained.

Since methanol is a direct reaction product of hydrogen and carbon monoxide, it is theoretically possible by using an excess of carbon monoxide in the original water gas mixture to form first methanol and then acetic acid or ester in one operation. With this end in view, catalysts composed of metals or their compounds, i.e. of nickel, chromium, cobalt, copper, cadmium, or manganese, have been patented.[104] Catalysts similar to those proposed for the carbon monoxide-methanol reaction and comprising the oxides of copper, tin, lead, the acetate of copper, or the methylates of aluminum or tin, or mixtures have been claimed for the same reaction at pressures of 150 to 200 atmospheres and at about 300° C.[104c]

It is interesting to note that some of the earliest claims to processes capable of yielding oxygenated organic compounds from water gas mixtures included the formation of acids and esters.* Indeed, it is probable that the subsequent success attained by the leaders in the field in directing the reactions exclusively to methanol formation served as a stimulus to those who had hopes of forming acids and esters directly.

Claims [105] have been made for the formation of ketene from mixtures of hydrogen and carbon monoxide in the presence of such catalysts as the oxides of zinc, copper, or chromium, the chromates of zinc or copper, zinc aluminates, potassium zincate, or mixtures at temperatures below 400° to 450° C. and pressures of 200 atmospheres.

$$3CO + H_2 = CO_2 + CH_2CO.$$
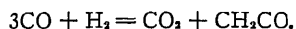
If ketene formation occurs it is obvious that the reaction does not occur as written. It is conceivable that the intermediate formation of methanol and acetic acid followed by the dehydrating of the acetic acid could lead

[103] Brit. Pat. 308,666 (1930) I. G. Farbenind.
[104] a. French Pat. 681,958 (1929) Soc. Française de Catalyse Generalisée; b. Brit. Pat. 313,467 (1928) I. G. Farbenind; c. Brit. Pat. 262,832 (1925) Dreyfus.
* *See* Chapter IV.
[105] U. S. Pat. 1,773,970 (1930) Dreyfus; *see also* Brit. Pat. 273,622 (1926) Dreyfus.

to the formation of ketene.[106] Carbon dioxide could be accounted for by the reaction of the evolved water with the excess carbon monoxide to form hydrogen and carbon dioxide. The temperature necessary for the splitting of acetic acid into ketene is so high that secondary decomposition usually occurs with formation of ethylene.

The Oxidation of Acetaldehyde

Although acetic acid has been obtained in the oxidation of ethanol in one operation, the yields are small [71] and acetic acid is generally obtained by oxidation methods from acetaldehyde which may have been obtained either from the hydration of acetylene or the oxidation of alcohol.[107]

While acetaldehyde is described in the literature as a substance which is readily oxidized by the oxygen of the air to give acetic acid, the production of acetic acid in large quantities and on a commercial scale by means of this transformation has presented very great difficulties. This is due to the fact that acetaldehyde combines directly with oxygen to give a colorless liquid which has a peculiar and indefinable odor and which is very unstable. This product, which is not acetic acid, has a composition corresponding to $CH_3CHO.O_2$. It is called peracetic acid and may be regarded as the acetyl derivative of hydrogen peroxide, i.e., $CH_3CO.OOH$. The fact that it decomposes violently with such a development of heat that the preparation of even a small amount is extremely dangerous, has made the oxidation of acetaldehyde a problem requiring extended and careful investigation.

As a result of this it has now been established that peracetic acid if subjected to heat alone decomposes according to the equation

$$CH_3CO_3H = CH_3COOH + O,$$

whereas in the presence of an excess of acetaldehyde, the decomposition takes place in the following way:

$$CH_3CO_3H + CH_3CHO = 2CH_3COOH.$$

In both cases pure concentrated acetic acid is formed. The temperature at which peracetic acid breaks down is somewhere in the vicinity of 100° C. (probably 80° to 100° C.) and the only safe way to proceed in the oxidation of acetaldehyde is, therefore, either to maintain the temperature at all points throughout the reacting masses sufficiently high to insure the decomposition of peracetic acid as rapidly as it is formed, or to secure the same result at a lower temperature by a mechanical agitation of the

[106] Hurd and Martin, *J. Am. Chem. Soc.* 51, 3614-7 (1929).
[107] a. Arkenasy, Leiser, and Grünstein, *Z. Elektrochem.* 15, 846 (1909); b. Kiss and Demeny, *Rec. trav. chim.* 43, 221 (1924); c. Neumann and Schneider, *Z. angew. Chem.* 33, 189 (1920); d. Fester and Berraz, *Anales assoc. quim. Argentina* 15, 210 (1927); e. Marshall, *Chem. Trade J.* 65, 361 (1919); f. Rooney, *Chem. Met. Eng.* 22, 847 (1920); g. Hutin, *Rev. chim. ind.* 30, 247 (1921); h. Deschiens, *Chimie et Industrie* 5, 239, 398, 518 (1921); i. Meingast, *Chem. Ztg.* 49, 446 (1925); 52, No. 36 (1928).

oxidizing mixture in the presence of some catalyst which possesses the power of greatly accelerating this decomposition. In neither case is the problem so simple as might appear at first sight and a relatively large number of patents have been issued which describe different methods for eliminating this difficulty during the process of oxidizing acetaldehyde in both the liquid and the vapor phases.

It was known as early as 1853 [108] that the oxidation of acetaldehyde by the air took place slowly under ordinary conditions but that it could be accelerated by the presence of platinum black. Since then numerous other metals and their compounds have been observed to exercise an accelerating effect upon this reaction.

If a *moist* aldehyde is shaken with palladium black, acid and hydrogen (combined with the palladium) are obtained.[109] If air is admitted the hydrogen is used up and the dehydrogenation can proceed further. Benzoquinone, methylene blue, and other quinoid compounds have been found to play the same part as atmospheric oxygen in the reaction in using up the released hydrogen. Dry silver oxide does not react with anhydrous acetaldehyde, whereas in the presence of moisture energetic oxidation at once sets in. The same has been found to hold for the chlorinated aldehydes, $CCl_3.CHO$ and $CCl_3.CHO.H_2O$. These observations led Wieland to the conclusion that the phenomenon was essentially one of dehydrogenation:

$$R.CHO.H_2O = [R.CH(OH)_2] = R.C\underset{\displaystyle OH}{\overset{\displaystyle O}{<}} + H_2$$

$$[R.CH(OH)_2] + O = RC\underset{\displaystyle OH}{\overset{\displaystyle O}{<}} + H_2O.$$
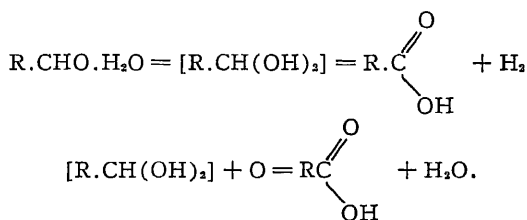
In the presence of a catalyst such as palladium black autoxidation, consisting of the introduction of oxygen into the molecule, or dehydrogenation would be catalyzed to different extents depending on whether or not water was present, the dehydrogenation reaction occurring only in the presence of water. In the case of benzaldehyde the velocity of oxidation is practically the same for either case. With acetaldehyde the rate of oxidation is decreased in the presence of water, a fact explained by Wieland on the basis of the existence of an equilibrium between the hydrated and anhydrous forms and the fact that only the latter form undergoes the rapid direct oxidation and the former the slower dehydrogenation process.

When acetaldehyde is employed in the liquid phase,[110] the procedure in general consists in passing oxygen or air into the pure substance or its

[108] Gmelin, Handbook of Chemistry, Vol. VIII, Cavendish Soc. Ed., p. 277, 1853.
[109] Wieland, *Ber.* **45**, 2606-15 (1912).
[110] *Compare* Conant, Aston, and Tongberg, *J. Am. Chem. Soc.* **52**, 407-19 (1930).

acetic acid solution under constant stirring at temperatures which may vary from 10° to 100° C., with or without the presence of catalysts, and under either atmospheric or high pressures.

In the first description of the technical process catalysts of vanadium, uranium, or iron were recommended.[111] Other catalysts that have been recommended consist of the oxides of iron, uranium, etc., with or without the addition of sodium acetate [112]; cerium, vanadium, chromium or copper oxides, acetates, manganates, etc.[113]; inorganic matter present in animal charcoal [114]; kaolin, with or without the presence of sodium acetate [115]; kieselguhr (infusorial earth) [116]; water with catalysts present [117]; and without.[118] Finally, compounds of manganese are very particularly recommended as superior to all other catalysts because of the fact that they not only accelerate the reaction but obviate all danger from explosions due to local accumulations of peracetic acid.[119] However, cobalt acetate is superior to the salts of either nickel, manganese, vanadium, cerium, iron, or chromium as a liquid phase catalyst.[120]

In liquid phase oxidation of abietic acid,[121] the abietates of cadmium, zinc, copper, magnesium, lead and sodium dissolved in the solution containing the acid, acted as oxidation retardants. On the other hand, the abietates of nickel, manganese, iron, mercury, and cobalt acted as positive catalysts, with the cobalt compound the most active. This may be due to the fact that the cobaltic ion has the highest oxidation potential of the metals named above,[122] and that the rôle of the catalyst in these processes is one of an oxygen exchanger. When fully oxidized these catalysts are capable of becoming reduced to a lower stage by the oxidation of an organic molecule or of hydrogen and then of being reoxidized by oxygen. When sufficiently active catalysts are used, so that there is no danger of explosion of peracetic acid, the use of pressure is very effective in increasing the yield of acetic acid.

In a batch operation process, aldehyde having 0.5 per cent of manganese acetate dissolved in it is warmed to 20° to 25° C. in an autoclave. Air is then introduced until the total pressure rises to from 75 to 120 pounds per square inch. The temperature rises to about 65° C. during

[111] Ger. Pat. 261,589 (1911) Grünstein, assr. to Chem. Fabrik Griesheim.
[112] Brit. Pat. 156,916 (1919) Dreyfus; Brit. Pat. 17,424 (1913) Johnson assr. to Chem. Fabrik Griesheim (same as U.S. Pat. 1,081,959 (1913) Grünstein).
[113] Fr. Pat. 479,656 (1914) Dreyfus; Fr. Pat. 471,255 (1914); Brit. Pat. 10,377 (1914); and Ger. Pat. 28,640 (1915) all to Meister, Lucius and Brüning.
[114] Brit. Pat. 154,680 (1919) Dreyfus.
[115] Brit. Pat. 154,304 (1919) British Cellulose and Chem. Mfg. Co. (pressure up to 7 atmospheres).
[116] Ger. Pat. 299,782 (1921) Fr. Baeyer and Co.
[117] Brit. Pat. 156,146 (1920) Otto Traun's Forschungs Laboratorium.
[118] Ger. Pat. 287,360 (1913) Behrens.
[119] Fr. Pat. 460,971 (1913); Ger. Pat. 305,550 (1914) Consortium f. Elektro-Chem. Industrie. Also Brit. Pat. 17,016 (1911) Consortium f. Elektro-Chem. Industrie; U.S. Pat. 1,179,420 (1916) Galitzenstein and Mugden; U.S. Pat. 1,410,207 (1922) and 1,481,326 ((924) Matheson; also compare Brit. Pat. 132,558 (1919) Matheson. See also Ger. Pat. 294,724 (1914); 296,282 (1914) Badische Anilin u. Soda Fabrik on liquid phase oxidation of acetaldehyde.
[120] King, Swann, Keyes, Ind. Eng. Chem. 21, 1227-31 (1929).
[121] Dupont and Levy, Compt. rend. 189, 920-2 (1929).
[122] Creighton and Fink, "Principles and Applications of Electrochemistry." New York, John Wiley and Sons, Inc., 1924, Vol. I, p. 229.

the admission of the air and the oxidation is rapidly completed. Acetic acid of 98 to 99.5 per cent purity is produced in yields varying from 88 to 95 per cent of theoretical. It is not necessary to have acetic acid present at the start as with many of the other processes.[123]

Estimated yields show the consumption of 170 kg. of calcium carbide representing 100 kg. of coke and 600 K.w.h. of electrical energy per 100 Kg. of acetic acid formed.[124]

Relatively little research on the oxidation of acetaldehyde by oxygen in the vapor phase has been recorded in either the general or patent literature. Apparatus suitable for this and other similar oxidation reactions is described as being heated electrically either by use of a catalyst which itself acts as a conductor or by use of a catalyst which has conducting material incorporated in it.[125] The reaction temperature is said to be maintained in this way at 100° C. Other patents dealing with this transformation have been taken out by Dreyfus.[126] The first of these describes the passage of acetaldehyde vapor mixed with air over platinum, or other bodies known to act as oxygen carriers in this reaction, at temperatures above the boiling point of acetic acid and below 400° C. Under these conditions the acetic acid remains in the form of a vapor and is not condensed in the reaction vessel. Later the observation was made that the rapidity of oxidation is greatest between 150° and 200° C. and that at this temperature there is a complete transformation into acetic acid without decomposition products. This may be brought about in the presence of catalysts which present a large surface (i.e., copper gauze, waste glass or porcelain mixed with oxides of chromium, uranium, vanadium, cerium) or even by employing glass balls or other non-catalytic material so long as this affords a large surface and insures a wide path for the oxidizing mixture. The procedure consists in passing the gases through tubes constructed of copper-iron, chromium lined iron, pottery, or other acid resisting materials, of any length (i.e., 50 to 100 meters) arranged in a bath of oil which is maintained at 150° to 200° C. According to the third of these patents the transformation is brought about in a reaction chamber which is provided with agitators in order to effect a thorough mixing of the reacting gases.

The oxidation of acetaldehyde may also be carried out at temperatures of 80° to 100° C. by means of oxidation towers either in the presence or absence of a catalyst.[127] Under these conditions peracetic acid is normally decomposed as rapidly as it is formed. In towers wetted with acetic acid and containing catalysts such as vanadium pentoxide, uranium oxide, roasted ferroso-ferric oxide, etc., the reaction between the aldehyde vapors and air is very rapid and complete, and temperatures as low as 30° to

[123] Brit. Pat. 132,558 (1919); U.S. Pats. 1,410,207 (1922); 1,481,326 (1923) Matheson (*see also Chem. Trade J.* 63, 283-4 (1918)).
[124] Schlumberger, *Z. angew. Chem.* 40, 141 (1927); Hess, *Chem. Ind. Germany* 52, 3 (1929).
[125] Brit. Pat. 126,279 (1919) Gilliard, Monnet and Cartier, assrs. to Societe Chimique des Usines du Rhone.
[126] Brit. Pat. 105,065 (1917); 108,459 (1918); 110,545 (1919) Dreyfus.
[127] U.S. Pat. 1,081,959 (1913); Brit. Pat. 17,424 (1911) Griesheim-Elektron.

60° C. may be used without impairing the efficiency of operation. When working without a catalyst, however, accidental cooling of the towers may lead to an accumulation of peracetic acid with the accompanying danger of an explosion. This possibility is eliminated by use of an arrangement which is described in a later patent.[128] According to the specifications the liquid products of the reaction are caused to flow out of the catalytic chamber in a continuous manner and as rapidly as formed. On leaving the oxidation towers they are passed directly into a supplementary heating apparatus which is maintained at such a temperature that any traces of peracetic acid, if present, may be instantly destroyed. In this way it is stated that all possible dangers of an explosion are completely avoided. The use of reaction vessels filled with solid diluents insures a more thorough and uniform contact and heating of the reactants and suppresses explosion dangers.[129]

The known fact that pure acetaldehyde in water solution will, in the presence of palladium black, react to give acetic acid and palladium hydride,[130] has not been utilized for vapor phase operations on a commercial scale.

Oxidation of Ether

As in the classical dehydration of alcohol in the presence of sulfuric acid,[131] to form ether, the same transformation may be accomplished under certain conditions in the vapor phase by passing ethanol vapors over dehydrating catalysts as has already been shown. Although this particular decomposition does not occur in the oxidation of ethanol over dehydrogenating catalysts, yet the presence of formaldehyde in the products obtained when certain border line catalysts have been used might indicate that the initial dehydration which occurs had gone partly to formation of ether which subsequently oxidized or decomposed.

Although no commercial value is attached to the vapor phase oxidation of ethyl ether to acetaldehyde and formaldehyde, it is nevertheless of interest to investigate some of the early work.

Ethyl ether vaporized and mixed with air is oxidized very readily in the presence of a copper gauze catalyst preceded in the reaction tube by a few pieces of platinum impregnated pumice (Zündpille).[132] When the air-vapor mixture is preheated to 100° C. and passed into the reaction chamber the catalyst begins to glow without the application of external heat. Besides formaldehyde and acetaldehyde the exit gases contain ethylene, carbon monoxide, hydrogen, as well as carbon dioxide and nitrogen from the air.

[128] U.S. Pat. 1,409,089 (1922) Guyot, assr. to La Compagnie des Products Chimique D'alais et de Camarque. *Also compare* Brit. Pat. 130,651 (1919) by the same company.
[129] Swedish Pat. 62,474 (1927); U.S. Pat. 1,601,891 (1926) Stockholms Superfosfat Fab. A-B.
[130] *Compare* Norris "The Principles of Organic Chemistry," New York, McGraw-Hill Book Co., 1922, p. 195.
[131] Mitscherlich, *Pogg. Ann.* 31, 273 (1834).
[132] Orloff, *J. Russ. Phys. Chem. Soc.* 40, 799-800 (1908)

$$(C_2H_5)_2O + O_2 = 2C_2H_4O + H_2O$$
$$(C_2H_5)_2O = 2C_2H_4 + H_2O$$
$$C_2H_4 + O_2 = 2HC_2O.$$
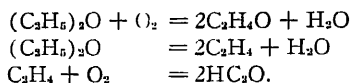
This oxidation has some practical value in that mixtures of ether vapor and air may be passed over the catalysts used in the oxidation of alcohols when they do not become heated spontaneously by the alcohol oxidation. In this way external heating may be dispensed with, since the ether-air mixture oxidized at a lower initial temperature and the heat generated soon raises the catalyst temperature to the proper point.

Catalysts formed by igniting asbestos threads that have been impregnated with nitrates of iron, nickel, cobalt, chromium, copper, manganese, cerium, or silver will also ignite ether-air mixtures with formation of acetaldehyde.[133]

When a stream of air is passed over liquid ether and then over a red hot platinum spiral, hydrogen peroxide may be continuously obtained by scrubbing the vapors with water. Ether apparently forms a peroxide under the conditions, which is decomposed by the scrubbing water. If the products are condensed and the liquid product slowly evaporated over sulfuric acid, a crystalline material remains which is slowly volatile and is capable of detonation. It is also capable of liberating iodine from potassium iodide.[134] On the other hand, if red hot pumice is substituted for the platinum catalyst, the scrubbing water shows no peroxide formation, and aldehyde and acetone are the chief products.[135]

[133] Matignon and Trannoy, *Compt. rend.* 142, 1210-11 (1906).
[134] Legler, *Liebig's Ann.* 217, 381-6 (1883); *Ber.* 14, 602-4 (1881).
[135] Dunstan and Dymond, *J. Chem. Soc.* (London) 57, 585-6 (1890).

Chapter IV

Reactions Involved in the Synthesis of Hydrocarbons and Alcohols from Water Gas

Before the oxidation reactions of ethanol and the higher aliphatic alcohols were reviewed in Chapter III, the thermal decompositions of these substances in the presence of various catalysts were detailed in Chapter II with the view of pointing out some of the difficulties in the way of direct oxidation processes. Although involving simpler substances, the oxidation of methanol to formaldehyde, and the oxidation of methane to various oxygenated organic compounds as well as to hydrogen are complicated by numerous side reactions and decompositions. In the case of these two substances, methane and methanol, it is more desirable to study the thermal stability of the substances and the intermediate compounds from the viewpoint of synthesis rather than decomposition as was the case with the higher alcohols. The reactions involved, and the catalysts used will be given primary consideration and the present day commercial practices involved in methanol and higher alcohol synthesis will be left to a more appropriate discussion in some book on high pressure processes.

In connection with the oxidation of methanol and also of methane it has been noted that in addition to the desired intermediate products of oxidation, mixtures of carbon monoxide, carbon dioxide, hydrogen and water are always formed, sometimes practically to the exclusion of intermediate compounds. These substances represent the products of destructive processes (i.e., manufacturing losses) and it is therefore desirable in all cases that their formation should be eliminated or suppressed as far as possible. To do this a very detailed knowledge of the physical and chemical properties of these substances, their modes of formation, stability, equilibrium relationships, etc., is necessary. Since these four compounds, together with small quantities of other substances, are present in the so-called catalytic water-gas process, the investigation of their interrelationships has, almost from the beginning, been associated with a study of what has come to be known as "the water-gas equilibrium," which applies primarily to the gaseous system; carbon monoxide, carbon dioxide, hydrogen and water.[1] However, an extended study of this system has led to a recognition of the fact that at different temperatures and pressures various other gaseous systems may arise as the result of interaction be-

[1] Sabatier and Reid, "Catalysis in Organic Chemistry," New York, D. van Nostrand Co., Inc., 1922, p. 398.

tween the components represented above, their decompositions, and finally the progressive changes which may then occur in the products thus formed.[2] Among reactions of this type the following have perhaps been most carefully studied:

$$
\begin{aligned}
&\text{(a)} \quad C + 2H_2 = CH_4 \\
&\text{(b)} \quad 2CO = C + CO_2 \\
&\text{(c)} \quad CO + H_2O = HCOOH = CO_2 + H_2 \\
&\text{(d)} \quad CO + 3H_2 = CH_4 + H_2O \\
&\text{(e)} \quad 2CO + 2H_2 = CH_4 + CO_2 \\
&\text{(f)} \quad CO_2 + 4H_2 = CH_4 + 2H_2O \\
&\text{(g)} \quad 6CO + 4H_2 = C_3H_8 + 3CO_2 \\
&\text{(h)} \quad 3CO + 7H_2 = C_3H_8 + 3H_2O \\
&\text{(i)} \quad 4CO + 2H_2 = C_2H_4 + 2CO_2 \\
&\text{(j)} \quad 2CO + 4H_2 = C_2H_4 + 2H_2O \\
&\text{(k)} \quad CO + H_2 = HCHO \\
&\text{(l)} \quad CO + 2H_2 = HCHO + H_2 = CH_3OH \\
&\text{(m)} \quad 2CO + 4H_2 = C_2H_5OH + H_2O \\
&\text{(n)} \quad 2CO + 2H_2 = CH_3COOH.
\end{aligned}
$$

Synthesis of Methane and Other Aliphatic Hydrocarbons

Mixtures of carbon monoxide, carbon dioxide, hydrogen and water as formed by the reaction of steam on hot carbon are frequently found to contain methane. Methane formation may result from a variety of different reactions and its quantity depends upon the condition of the experiment; i.e., temperature, pressure, the relative proportions of the gases, and the catalysts present. The phenomena involved in the formation of methane have been the subject of investigations which have extended over a long period of time and which have been undertaken largely with two objects in mind: first, the enrichment of water-gas for illuminating purposes, and second, the utilization of coal as a source of liquid fuels.[3] It seems desirable at this point to review briefly the early history of these developments.[4]

The fact that a combustible gas was produced by passing steam over coke at red heat was first observed by Fontana in 1780, but the first analysis of this gas was made by Clement and Desormes[5] in 1802 and the first expression of its mode of formation, i.e.,

$$C + H_2O = CO + H_2$$

was offered by Gingembre in 1816. In 1838 the decomposition of water by carbon was denied by Longchamp,[6] but objections to his statements

[2] Smith, *Ind. Eng. Chem.* 19, 801 (1927). (Equilibrium Conditions.)
[3] Malisoff and Egloff, *J. Phys. Chem.* 22, 568-70 (1922).
[4] Compare (a) Vignon, *Ann. chim. phys.* (9) 15, 42-45 (1921) and (b) Fischer, Tropsch and Delthey, *Brennstoff Chem.* 6, 265-7 (1925).
[5] Clement and Desormes, "Chaleur specifiques des Gaz," 1802, Paris-Dijon $H_2 = 56.22\%$, $CO = 28.96\%$, $CO_2 = 14.68\%$; $CH = 0.49\%$.
[6] Longchamp, *Compt. rend.* 6, 178 (1838).

were brought forward in the same year by Gay-Lussac and Selligue.[7] Following this, investigations were undertaken by Bunsen,[8] and by Langlois,[9] as a result of which marked variations were reported in the relative percentages of carbon monoxide, carbon dioxide, hydrogen and methane, which were found to be present in the gas mixture under different conditions. The direct synthesis of methane from carbon monoxide and hydrogen was observed some years later by Brodie,[10] who found that the action of electricity on carbon monoxide and hydrogen in an induction tube resulted after five hours in the appearance of 6 per cent methane in the gas mixture. Further study of the water gas system by Gautier [11] at temperatures between 1200° and 1250° C. led him to the conclusion that the system is in equilibrium when the volume relationships are as follows: $CO : H_2O : 2H_2 : 2CO_2 = 2 : 2 : 4 : 4$. An investigation [12] of the action of hydrogen and carbon monoxide at temperatures between 300° and 1250° C. showed that these substances react to give carbon dioxide and water in small quantities, no carbon and traces of methane. The latter substance was observed to form in relatively smaller quantities when *dry* carbon monoxide and hydrogen were heated than when water-gas was used.[10] This work, which was purely thermochemical in character, afforded a foundation for extended research by Vignon.[4a, 13]

Vignon found that technical water gas contains a larger quantity of methane than was to be expected on the basis of Gautier's results and in seeking to account for this he arrived at the hypothesis that this higher percentage of methane was due to the catalytic action of minerals present in coke. Since ash was formed in amounts equal to 10.60 per cent of the coke and since calcium carbonate represented 7.33 per cent of this, Vignon assumed that the presence of lime in coke was primarily responsible for the catalysis. To verify this assumption he undertook a series of parallel experiments in which water-gas was prepared by passing steam over (a) carbon obtained from sugar; (b) carbon obtained from coal. Both forms of carbon were studied as to relative percentage of ash, etc. In the first case the resulting gas was found to contain less than one per cent methane and in the second case quantities varying from one to three per cent methane were obtained. Following this a series of experiments was carried on in which steam was passed over calcium oxide and carbon mixtures at temperatures around 1000° C. The results of these experiments showed that by increasing the ratio of CaO : C from 1 : 10 up to 1 : 2, yields of methane varying from 8 per cent to 20 per cent could be obtained. The mechanism of the process was interpreted by supposing that the primary product of the reaction was calcium formate and that

[7] Gay-Lussac and Selligue, *ibid.* 6, 180 and 207 (1838).
[8] Bunsen, *Ann. chim. phys.* (3) 38, 356 (1853).
[9] Langlois, *ibid.* (4) 2, 322 (1857).
[10] Brodie, *Proc. Roy. Soc.* 21, 245 (1873); *Ann.* 169, 270 (1873).
[11] Gautier, *Compt. rend.* 142, 1382 (1906).
[12] Gautier, *ibid.* 150, 1564 (1910).
[13] For the effect of the ash content of coke on the water-gas equilibrium, *compare* (a) Gwosdz, *Z. anorg. Chem.* 31, 137 (1918); (b) Taylor and Neville, *J. Am. Chem. Soc.* 43, 2055 (1921).

this subsequently decomposed in the presence of calcium oxide to give methane. While this explanation is somewhat involved and subject to question, the research itself opened up valuable lines of investigation as to the catalytic effect of alkaline substances in promoting various organic reactions in the vapor phase. A discussion of the later developments in this field will, however, be deferred for the moment since it seems desirable at this point to call attention to the effect produced by a quite different group of catalysts—namely, the metals, upon the system $CO + H_2$ or its equilibrium mixtures as represented in water-gas.

The catalytic action of nickel, cobalt, platinum, palladium, copper and iron in finely divided condition upon mixtures of carbon monoxide and hydrogen was investigated as early as 1902 by Sabatier and Senderens.[14, 1] Their experiments were conducted at different temperatures and under a variety of conditions and their results show that in the case of the hydrogenation of carbon monoxide, in the presence of finely divided nickel, the reaction:

$$CO + 3H_2 = CH_4 + H_2O$$
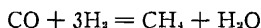
begins at 180° to 200° C. and proceeds rapidly and without complications at 230° to 250° C. Moreover, if care is taken that the temperature of 250° C. is not exceeded, the nickel is not impaired and retains its activity over long periods of time.[15] If the volumetric relations of $CO : H_2$ are maintained at $1 : 3$, the reaction is practically complete and almost pure methane is obtained in yields which correspond closely to theoretical values as calculated on the basis of the equation:

$$CO + 3H_2 = CH_4 + H_2O + 57100 \text{ cal.}$$

A comparative study of other catalysts showed that the action of cobalt was similar to that of nickel but required a higher temperature while negative results were obtained with platinum, palladium, copper, and iron. The discovery of the catalytic activity of finely divided nickel in promoting the synthesis of methane found immediate application in the various methods which were devised or suggested for the preparation of water-gas having a high methane content.[16]

It is interesting to note that although Sabatier and Senderens were unable to effect the reduction of carbon monoxide in the presence of iron and copper, Vignon, working in the wide temperature range of 250° to 1250° C. and using iron and copper in the form of filings, was able to demonstrate that both metals represent practical catalysts for use in this reduction. Vignon also found that the oxides of magnesium, silicon, and aluminum were applicable as catalysts in the reaction,[17] as shown in Table I.

[14] Sabatier and Senderens, *Compt. rend.* 134, 514 and 689 (1902); *Ann. chim. phys.* (8) 4, 424 (1905).
[15] For the hydrogenation of carbon monoxide in the presence of nickel and its oxides *see* Ipatiew. *J. prakt. Chem.* (2) 87, 479 (1913).
[16] Sabatier, Fr. Pat. 355,900 and 355,471 (1905).
[17] *Compt. rend.* 157, 131-34 (1913); *Ann. chim. phys.* (9) 15, 58 (1921).

TABLE I.—*Formation of Methane and Hydrogen from Carbon Monoxide and Steam.*

Inlet gas: practically pure carbon monoxide plus steam.

Catalyst	Temp. °C.	Exit Gas Composition H_2 Per Cent	CH_4 Per Cent
Ni (filings)	400	1.5	12.5
Cu (filings)	700	2.2	6.3
SiO_2	750	10.9	8.4
MgO	900	4.7	6.7
Fe (filings)	950	20.3	11.2
Al_2O_3	950	5.9	3.8

In examining the iron catalysts which had been used in hydrogenations of carbon monoxide, Vignon observed that when treated with acids they generated methane. This led him to the assumption that during the catalysis iron carbide was formed as the primary product of the reaction and that this was subsequently reduced to give methane.*

In summarizing the advances which had been made in a knowledge of equilibrium relationships in the system containing carbon monoxide, carbon dioxide, hydrogen and water up to 1915, or the beginning of what may be called the modern period, it may be said in general that two fundamentally important lines of investigation had been opened up, i.e., (a) the study of the catalytic action of metals in various states of aggregation as initiated by Sabatier and his co-workers, and (b) the study of the catalytic action of alkali as initiated by Vignon. Beginning with about 1913 great impetus was given to research in both fields.

The Action of Hydrogen on Carbon

The synthesis and decomposition of methane as expressed by the relation:

$$C + 2H_2 \rightleftarrows CH_4$$
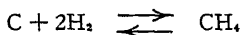
has been of interest to chemists from very early times. Thus Berthelot [18] in 1868 observed that the direct union of carbon and hydrogen takes place at the temperature of the electric arc. The quantitative investigation of the problems presented by methane chemistry was, however, not attempted until 1897 when Bone and Jerden [19] affected a direct synthesis by passing hydrogen over pure sugar carbon heated at about 1200° C. in a porcelain tube. The fact of the direct union of carbon and hydrogen at this temperature was denied by Berthelot,[20] who attempted to repeat the experiment in quartz tubes at 1300° C. and was unable to detect any methane. Berthelot also ventured the opinion that the formation of methane as described by the English chemists was due to impurities present in the

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* It is to be noted in this connection that the carbides of different metals are known to give different hydrocarbons, i.e. CH_4, C_2H_6, C_2H_4, etc. For a bibliography to the literature on this subject consult: *Abh. Kohle* 2, 303 (1917).

[18] Berthelot, *Ann. chim. phys.* (4) 13, 143 (1868).

[19] Bone and Jerden, *J. Chem. Soc.* 71, 41 (1897); 79, 1042 (1901).

[20] Berthelot, *Ann. chim. phys.* (8) 6, 183 (1905); *Compt. rend.* 140, 905 (1905).

carbon. This criticism of Berthelot's was sustained by Mayer and Alt-mayer,[21] who based their objections upon equilibrium data calculated on the basis of their investigations of the system in the presence of a nickel catalyst at temperatures ranging between 470° to 620° C. The work of Pring and Hutton,[22] who studied the same system at 1000° to 2800° C. in the absence of a catalyst, failed to allay these criticisms since although small quantities of methane were obtained at very high temperatures, the authors state that the per cent varied inversely with the purity of the carbon.

The fact of the actual synthesis of methane at temperatures of about 1200° C. and therefore of its relatively great stability at very high temperatures, was ultimately established beyond a doubt by Bone and Coward,[23] who repeated the earlier work with highly purified carbon and hydrogen and obtained an average yield of 73 per cent methane from about 0.1 gram carbon as the result of two parallel experiments.

In the same year Bone and Coward [24] further demonstrated the inherent stability of methane at temperatures up to 1200° C. as the result of investigations in regard to the decomposition of this substance at different temperatures ranging between 500° and 1200° C. They state that virtually no decomposition takes place below 700° C. These conclusions were confirmed by the investigations of Pring and Fairlie [25] which were undertaken first at high temperatures and ordinary pressure and later at high temperatures and pressures in the absence of a catalyst. A study of the system at ordinary pressures showed that methane formation occurred at all temperatures between 1200° and 1500° C. At these temperatures and at pressures up to 200 atmospheres, the same thing was observed, the effect of increased pressure being merely to increase the velocity of the reaction toward the formation of methane. They state, moreover, that no saturated hydrocarbons other than methane were formed at temperatures of 1100° and 2100° C. and at pressures up to 200 atmospheres. This is to be expected, of course, since no other saturated hydrocarbons are stable at these temperatures under the conditions.

The effect of catalysts upon the system has been the subject of extended investigation. Coquillon [26] observed that when methane was passed over palladium wire heated to redness, it decomposed to give a deposit of carbon. The direct synthesis of the substance in the presence of nickel at 200° C. was effected by Sabatier and Senderens [27] in 1907. They also observed that when the temperature was raised to 400° C., methane was no longer formed. In the same year Mayer and Altmayer [21] studied the synthesis of methane in the presence of nickel, cobalt and iron and found that at temperatures above 250° C. the substance decomposes

[21] Mayer and Altmayer, *Ber.* 40, 2134 (1907).
[22] Pring and Hutton, *J. Chem. Soc.* 89, 1591 (1906).
[23] Bone and Coward, *J. Chem. Soc.* 93, 1975 (1908); *compare also* 97, 1219 (1910).
[24] Bone and Coward, *J. Chem. Soc.* 93, 1197 (1908).
[25] Pring and Fairlie, *J. Chem. Soc.* 99, 1796 (1911); 101, 91 (1912).
[26] Coquillion, *Compt. rend.* 84. 1503-1504 (1877).
[27] Sabatier and Senderens, *Bull. soc. chim.* (4), 1, 107 (1907).

rapidly. For example, in contact with nickel 51.2 per cent methane was in equilibrium with its decomposition products at 536° C.; 24.7 per cent at 625°; 1.6 per cent at 850° C. In 1910 Pring [28] found that the presence of finely divided platinum accelerated the direct combination of carbon and hydrogen at 1200° C. Using a carbon rod coated with platinum, he obtained a value of 0.55 per cent methane. Catalysis in the presence of nickel and other metals has been investigated by Mayer, Henseling, Altmayer and Jacoby,[20] at ordinary pressures and over quite a wide range of temperatures; by Ipatiew [30] at high pressures and a temperature of about 500° C.; and by Coward and Wilson [31] at 650°, 850°, 1000° and 1100° C. The results obtained in the latter experiments are not in accord with those described by Mayer and Altmayer [21] and the suggestion was made that the German chemists may have mistaken carbon monoxide for methane in their product since it was considered improbable that appreciable quantities of methane could have been formed below 650° C. in the presence of a nickel catalyst.

Bone and Coward [24] found that the rate of decomposition of methane in the presence of porcelain was very low at temperatures below 700° C. Large surface exposure promoted the reaction, which apparently was reversible. Using as a basis the amount of dissociation in an empty tube Slater [32] found that silica, magnesia, alumina and baryta did not accelerate the reaction, and that copper, carborundum, graphite, charcoal, and iron did. The temperatures were between 900° and 1000° C., rather high for good comparison of catalytic surfaces.

The decomposition of methane in the presence of calcium oxide, copper-copper oxide, nickel-nickel oxide, and iron-iron oxide on asbestos, silica gel, and bone-black at temperatures of 600°, 700°, 760° and 780° C. has been studied by Cantelo.[33] Patents utilizing this decomposition for the production of pure hydrogen have been issued to Diffenback and Moldenhauer,[34a] Badische Anilin u. Soda Fabrik,[34b] to Herman [35] and others. Equilibrium constants for the system have been calculated by Pring, by Mayer and Altmayer, and by Cantelo, and by several subsequent workers. Thermodynamic relationships have been investigated by Keyes, Taylor and Smith.[36] A fairly extensive bibliography has also been compiled by Malisoff and Egloff [37] of references in the literature which describe the physical properties, physical-chemical constants and a wide range of other data applying to methane and to substances such as carbides, halides, cyanides, etc., which may be prepared from it.

[28] Pring. *J. Chem. Soc.* 97, 498 (1910).
[29] Mayer, Henseling, Altmayer and Jacoby, *J. Gasbeleucht* 52, 166, 194, 238, 242, 305, 324, 326 (1909).
[30] Ipatiew, *J. prakt. Chem.* (2) 87, 479-87 (1915); *J. Russ. Phys. Chem. Soc.* 45, 433 (1913).
[31] Coward and Wilson, *J. Chem. Soc.* 115, 1380-87 (1919).
[32] Slater, *J. Chem. Soc.* 109, 161 (1916).
[33] Cantelo. (a) *J. Phys. Chem.* 28, 1036-48 (1924); (b) *ibid.* 30, 1641-5 (1926).
[34] a. Dieffenbock and Moldenhauer, Ger. Pat. 223,406 (1909); b. Badische Anilin u. Soda Fabrik, Ger. Pat. 296.866 (1912).
[35] Herman. Ger. Pat. 303.881 (1919).
[36] Keyes, Taylor and Smith, *J. Math. Phys. Mass. Inst. Tech.* 1, 211-42 (1922).
[37] Malisoff and Egloff, *J. Phys. Chem.* 22, 529-74 (1918).

Randall and his coworkers [38] have very carefully determined the equilibrium experimentally and compared their results with those of earlier workers. The direct measurements gave results which agree with those obtained by indirect measurements. From the direct measurements the free energy change as a function of temperature for the reaction:

$$c(\text{graph.}) + 2H_2(g) = CH_4(g)$$
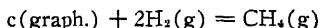
is represented as follows:

$$\Delta F = -14{,}343 + 11.1T \ln T - 0.00081T^2 + 0.0000006T^3 - 51.59T.$$

The results of all the investigations on the thermal stability of methane show it to be rather refractory. Temperatures as high as 700° C. are necessary before decomposition becomes active and long times of contact are required even then before marked dissociation to hydrogen and carbon occurs. The dissociation is largely reversible at all temperatures and has been found to be chiefly a surface-catalyzed reaction. Catalysts of nickel and iron have been found to be particularly active.
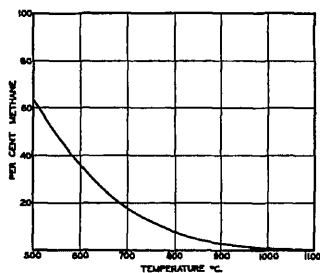
FIG. 5.—Methane present at equilibrium in the system: $C + 2H_2 \rightleftarrows CH_4$. (Cantelo.[33b])
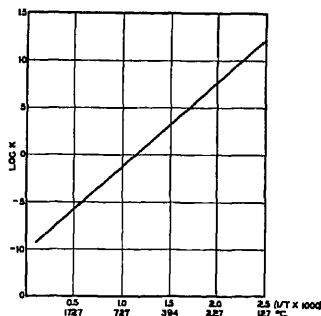
FIG. 6.—Log K as a function of temperature for the system: $CO_2(g) + 4H_2(g) \rightleftarrows CH_4(g) + 2H_2O(g)$ (from equation of Randall and Gerard[38a]).

Under suitable conditions methane forms higher liquid and solid hydrocarbons when heated.[39] These conditions have been found to be short times of contact on the order of less than one second and at temperatures of 1000° to 1200° C. The products may consist of acetylene, ethylene, ethane, higher olefins, benzene and higher aromatic hydrocarbons, carbon, and hydrogen.[40] However, as the temperature range in which these effects have been noted is much higher than is used in oxidation work an investigation of the process is not warranted here.

[38] a. Randall and Gerard, *Ind. Eng. Chem.* 20, 1335 (1928); b. Randall and Mohammad, *ibid.* 21, 1048-52 (1929).
[39] Fischer, *Brennstoff Chem.* 9, 309 (1928).
[40] a. Wheeler and Wood, *Fuel* 7, 535 (1928); b. Stanley and Nash. *J. Soc. Chem. Ind.* 48, 1-8T (1929); c. Egloff, Schaad, and Lowry, *J. Phys. Chem.* 34, 1617-1740 (1930).

Decarbonization of Carbon Monoxide

The decarbonization of carbon monoxide as represented by the equation:

$$2CO = CO_2 + C$$

was first obtained by Deville[41] in 1864. Five years later a comparative study of the catalyzing effect of nickel, cobalt, and iron upon the velocity of the reaction was undertaken by Bell.[42] The results which were obtained in the case of metallic iron showed that at temperatures of 250°, 400°, 500°, 600°, and 800° C., carbon was deposited in amounts corresponding to 4.7, 181, 95, 6, and 0.3 grams respectively, thus indicating that the higher temperatures were unfavorable for the decomposition of carbon monoxide to carbon. In comparing the relative activities of the metallic oxides with the corresponding activities of the metals, Bell came to the conclusion that at the various temperatures which were investigated, the oxides were as effective as the metals themselves. In 1901 Boudouard[43] studied the state of equilibrium of the system when in contact with nickel and iron at different temperatures and pressures. From the data which was obtained in this way equilibrium constants were calculated. Boudouard is authority for the statement that in the presence of finely divided iron, heated at 445° C., carbon monoxide is completely transformed into carbon dioxide in the course of a few hours. A few years later the results described by Bell and Boudouard were challenged by Schlenck and Zimmermann[44] and by Smith and Wolff,[45] respectively.

According to Sabatier and Senderens[46] the decomposition of carbon monoxide in the presence of nickel begins at 230° C. and increases rapidly up to 349° C., at which point decomposition is complete. Recent investigations of the effect of temperature on the dissociation equilibrium of this system in contact with nickel and other catalysts, have been undertaken by Rhead and Wheeler[47] and also by the United States Bureau of Mines[48] with the object of eliminating or minimizing the amounts of carbon dioxide formed during the process of producer gas manufacture. The effect of different catalysts on the rate of decomposition has also been studied by Taylor and Neville,[49] who include in their report a bibliography of some of the work which has been done as well as some of the patents which have been issued to cover various phases of the process.

Palladium on silica gel or charcoal has been found to promote the decarbonization of carbon monoxide,[50] whereas a nickel catalyst consisting

[41] Deville, *Compt. rend.* 59, 873 (1864); 60, 317 (1865).
[42] Bell, *J. Chem. Soc.* 22, 203 (1869).
[43] Boudouard, *Ann. chim. phys.* (7), 24, 5 (1901); *Compt. rend.* 130, 132 (1900).
[44] Schlenck and Zimmermann, *Ber.* 36, 1 (1903).
[45] Smith and Wolff, *Z. physik. Chem.* 45, 199 (1903).
[46] Sabatier and Senderens, *Bull. soc. chim.* (3) 29, 294 (1903).
[47] Rhead and Wheeler, *J. Chem. Soc.* 97, 2178 (1910); 99, 1140 (1911); 101, 831 (1912).
[48] a. *Bur. Mines Bull.* No. 17 (1911); *also compare* b. Mayer and Henseling, *J. Gasbeleucht,* 52, 167 and 194 (1909).
[49] Taylor and Neville, *J. Am. Chem. Soc.* 43, 2055-71 (1921).
[50] Fester and Brude, *Brennstoff Chem.* 5, 49 (1924).

of 73 per cent charcoal and 27 per cent nickel and made by carbonizing sugar and nickel acetate when used in the synthesis of hydrocarbons does not promote the reaction.[51]

The mechanism of the reaction which takes place in the presence of nickel as well as certain other of the metal catalysts, has been explained by assuming that metallic carbonyls are formed by the action of carbon monoxide on the metal and that these compounds represent intermediate products in the catalyses. Evidence in support of this theory has been brought forward by Mond, Langer and Quinke,[52] who studied the decomposition of carbon monoxide in contact with nickel at temperatures between 350° and 450° C. In examining the carbonized nickel catalyst at the end of the experiment these investigators discovered that when heated, it gave off a volatile inflammable nickel compound which could be condensed to a liquid and which was later identified as nickel carbonyl. Metals, such as nickel, cobalt, and iron, which form distinct metallic carbonyls are particularly active catalysts for the decomposition, a fact which adds weight to this theory.

Although the work of Boudouard gave the order of magnitude of the equilibrium for the reaction, it lacked certain refinements necessary for obtaining very accurate data. The work of Clement at the United States Bureau of Mines was concerned mainly with rates of reaction and is not sufficiently accurate for equilibria calculations. The very careful measurements of Rhead and Wheeler [47] have been used as the basis for the calculation of the free energy change [53] accompanying the reverse reaction:

$$C(\text{graph}) + CO_2 = 2CO.$$
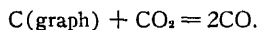
By use of this equation values for the equilibrium constant may be calculated as shown in Table II.

TABLE II.—*Equilibrium as a Function of Temperature for the Reaction:* $C + CO_2 \rightleftarrows 2CO$.

Temperature		$C + CO_2 \rightleftarrows 2CO$
° C.	° K	Log K
127	400	−13.62
327	600	− 5.90
527	800	− 2.04
727	1000	+ 0.252
927	1200	+ 1.769

These values indicate that there is a considerable tendency for carbon monoxide to decarbonize to carbon dioxide at temperatures in the range used in the ordinary vapor phase synthesis work, i.e., 300° to 650° C. At higher temperatures the tendency reverses and carbon dioxide reacts

[51] Chakravarty and Ghosh, *J. Indian Chem. Soc.* 2, 150, 157 (1925).
[52] Mond, Langer and Quinke, *Chem. News* 62, 97 (1890); *also compare J. Chem. Soc.* 97, 793 (1910); 121, 29 (1922).
[53] Lewis and Randall, "Thermodynamics and the Free Energies of Chemical Substances," New York, McGraw-Hill Book Co., 1923, p. 574.

with carbon to form carbon monoxide. However, this latter reaction is usually encountered only in furnace or gas producer operation, and the deposition of carbon from carbon monoxide is the only manifestation of the reaction encountered in the range of temperatures met with in ordinary oxidation work.

The Catalytic Oxidation of Carbon Monoxide by Steam

In the utilization of water-gas, which ordinarily comprises about 50 per cent hydrogen and 40 per cent carbon monoxide together with small amounts of carbon dioxide, nitrogen, etc., as a source of hydrogen in the synthesis of ammonia it is customary to oxidize the carbon monoxide to

$$CO + H_2O = CO_2 + H_2$$
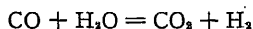
carbon dioxide by steam. Because of the importance of this reaction in the production of cheap hydrogen from coal and steam, it has received a considerable amount of attention. It has been found that the reaction is largely surface catalyzed and does not require a very specific catalyst. Hence, the equilibrium between the four substances involved may exist in any catalytic system in which they are present or are formed. Thus, in the synthesis of methane from hydrogen and carbon monoxide the reaction may lead to the formation of either water or carbon dioxide, or both. These products may be governed in the extent of their relative formation by the equilibrium existing through the water-gas catalytic reaction. The

$$2H_2 + 2CO = CH_4 + CO_2$$
$$3H_2 + CO = CH_4 + H_2O$$
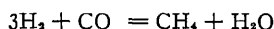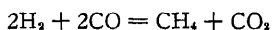
same is true of the case in which methane is acted on with steam or oxygen, where carbon dioxide and water are formed together with carbon monoxide and hydrogen.

The equilibrium for this reaction has been experimentally determined by Hahn[64] and by Haber and Richardt.[55] From the free energy changes of the reverse reaction[53] the equilibrium constant as a function of temperature may be expressed as:

$$4.57 \log K = \frac{10,100}{T} - 4.16 \log T + 0.00445T - 0.00000068T^2 - 0.54$$

where,

$$K = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}}$$

and T is in degrees Centigrade absolute. At low temperatures equilibrium is in favor of complete transformation to hydrogen and carbon monoxide, while at high temperatures the reaction reverses. At 450° C. only a small amount of carbon monoxide remains at equilibrium.

[64] Hahn, *Z. physik. Chem.* **44**, 513 (1903); **48**, 735 (1904).
[55] a. Haber and Richardt, *Z. anorg. Chem.* **38**, 5 (1904); *also* b. Partington and Schilling, *J. Soc. Chem. Ind.* **44**, 149T, 242T (1925).

The fact that the equilibrium relationships may be represented by the expression:

$$CO + H_2O \rightleftharpoons HCOOH \rightleftharpoons CO_2 + H_2$$
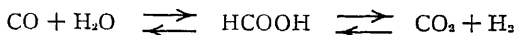
has led to a number of investigations.[56, 20, 4, 57] The accelerating action of platinum black on the decomposition of formic acid was observed by Mulder[58] in 1883 but it was not until almost thirty years later that Sabatier and Mailhe[59] directed general attention to the fact that decomposition of the simple acid:

(a) $HCOOH = CO_2 + H_2$ and
(b) $HCOOH = CO + H_2O$
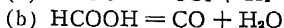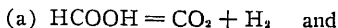
could be directed more or less definitely by the specific action of certain catalysts. For example, the velocity of the first reaction (a) was noticeably increased if the formic acid was heated in the presence of such metals as palladium, platinum, copper, cobalt, and nickel or in the presence of metallic oxides such as zinc and tin, while the second reaction (b) was favored by the presence of the oxides of titanium, tungsten, zirconium, aluminum, uranium, and silicon. In cases where the oxides of iron, manganese, chromium, molybdenum and cerium were used traces of formaldehyde appeared along with carbon oxides. Aldehyde formation was also observed when heating was conducted in the presence of lime, carbon, or Jena glass. Six years later a somewhat closer study of the activating effect of copper and nickel upon the dissociation, was undertaken by Mailhe.[60]

In 1920 Armstrong and Hilditch[61] investigated the action of solid surfaces on the reaction:

$$CO + H_2O = CO_2 + H_2$$
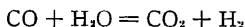
and found that in the presence of copper the reaction began at 220° C. and proceeded actively between that temperature and 300° C. In the presence of ferric oxide the initial temperature of the reaction was higher (250° C.) and reaction active below 400° C. At temperatures of about 600° C., however, the oxidation was found to be much more complete than in the presence of copper. A detailed and exhaustive study of the influence of different catalysts acting within definite temperature ranges has been undertaken by Hinshelwood, Hartley, Topley and others.[62] Adkins and Nissen[63] studied the effects of alumina catalysts prepared in different ways on the decomposition of formic acid, and concluded that the distances separating the molecules of alumina, as determined by the method

[56] Wieland, *Ber.* **45**, 679-685 (1912); *ibid.* **45**, 2606-15 (1912)
[57] U.S. Pats. 1,740,140-1 (1929) Arsem, assr. to Commercial Solvents Corp.
[58] Mulder, *Rec. trav. chim.* **2**, 44 (1883).
[59] Sabatier and Mailhe, *Compt. rend.* **152**, 1212-15 (1911).
[60] Mailhe, *Bull. soc. chim.* (4) **21**, 61-64 (1917).
[61] Armstrong and Hilditch. *Proc. Roy. Soc.* **97A**, 265-73 (1920).
[62] Hinshelwood, Hartley, Topley and others, *Proc. Roy. Soc.* **100A**, 575-81 (1922); *J. Chem. Soc.* **121**, 1668 (1922); **123**, 1014 and 1333 (1923).
[63] Adkins and Nissen, *J. Am. Chem. Soc.* **45**, 809-15 (1923).

of preparation, were the important factors in defining the activity and selectivity of the catalyst.

In the industrial utilization of this process for the conversion of carbon monoxide to carbon dioxide with formation of an equivalent amount of hydrogen, catalysts of iron promoted with oxides of cerium, aluminum, etc., are employed.[64]

The Reduction of Carbon Monoxide by Hydrogen to Form Methane

The formation of methane from mixtures of hydrogen and carbon monoxide with the simultaneous liberation of water or carbon dioxide represents the reversal of the reactions which occur during the production of hydrogen from methane by acting on it with water or carbon dioxide.* Since the reactions occur in either direction they are reversible and an equilibrium state may exist at any temperature. The free energy change for these reactions

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$$
$$2CO + 2H_2 \rightleftharpoons CH_4 + CO_2$$
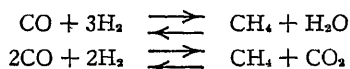
is such that at low temperatures equilibrium is in favor of methane formation and at high temperatures is in favor of methane decomposition. Thus, in the case of the reaction of steam on methane to form carbon monoxide and hydrogen, a temperature of about 350° C. is necessary before appreciable reaction can occur and a temperature of 1000° C. is necessary for the practically complete destruction of methane. This means that some methane could be formed at any temperature up to about 1000° C. if the true equilibrium could be reached in the hydrogen-carbon monoxide mixture, and that at temperatures below 350° C. equilibrium is very favorable for methane formation.

In the early experiments that were made with water-gas mixtures in attempts to synthesize valuable organic liquids, methane apparently was the only product obtained until the effect of pressure was understood, after which the progress toward methanol synthesis was rapid. Aside from the work that had to do quite largely with the production of methane for the enrichment of water-gas or other low calorific value gaseous mixtures in countries without cheap oil, considerable attention has been paid to a study of the effects of various catalysts on the synthesis from the viewpoint of perfecting the methanol and higher alcohol syntheses. Processes have, at the same time, been proposed for the synthesis of liquid fuels from water-gas mixtures in an attempt to produce motor fuels from cheap coal.

This work is of interest in the present case because it has shown the effects of various catalytic materials at different temperatures on some of the various reactions that may occur in processes involving oxidation and decomposition of methane.

[64] a. Evans and Newton, *Ind. Eng. Chem.* 18, 513 (1926); b. Taylor, "Industrial Hydrogen," New York Chemical Catalog, Inc., 1921, p. 68; c. Ullmann's "Enzyklopädie der Technischen Chemie," Berlin, 1928, p. 378.
* *Cf.* Chapter IX.

Many investigations of the synthesis of methane from carbon monoxide-hydrogen mixtures represent in part a repetition of earlier work and have been undertaken with a view to defining the particular conditions of a given reaction with greater accuracy. The early researches of Sabatier led to a more thorough and precise examination of catalytic effects.[65] Thus, the catalytic effects of nickel, cobalt, and iron in different physical states, and at different temperatures and pressures have been investigated by Mayer, Henseling, Jacoby, and Altmayer [66] and also by Armstrong and Hilditch.[67] The latter workers showed in particular that among metals, nickel represents the best catalyst, iron is slow, palladium and platinum only slightly active and silver inactive. They also demonstrated that alumina is an excellent promoter for hydrogenations with nickel and iron. This latter fact is also supported by the observations of Medsforth,[68] who stated that 15 per cent alumina added to a nickel catalyst increased the velocity of hydrogenation to fourteen times that obtainable with pure nickel. Medsforth also recommended the use of ceria, thoria, and silica as promoters for nickel. The promoters such as alumina, thoria, and silica are all active dehydrating agents and this property has been attributed to give the increased reaction rates that are obtainable. With nickel alone as a catalyst, the hydrogenation of carbon monoxide to a possible hydroxy compound is accelerated since this metal is an active hydrogenating catalyst. The dehydration of this hydroxy compound is not affected by nickel. The use of dehydrating catalysts as promoters for nickel, however, results in the rapid dehydration and consequent rapid reaction rate of methane formation. It is noteworthy that the same oxides which promote nickel catalysts for the formation of methane from hydrogen and carbon monoxide also promote the iron catalysts which are used in the synthesis of ammonia from hydrogen and nitrogen. In this latter case the explanation for the promotion action must necessarily be different, and it has been postulated that the oxides are effective through a colloidal chemical action in preventing the agglomeration of active iron atoms during the reduction of the mixture of oxides. In this way the active atoms or "points" are left in an unsaturated condition, so that they have a higher energy level than the ordinary iron and can function toward accelerating reaction.[69] That such a mechanism holds true for the case of the nickel catalysts also is by no means untenable.

According to Chakravarty and Ghosh [70] of the two possible hydrogenations for carbon monoxide:

$$\text{(a)} \quad 2CO + 2H_2 = CO_2 + CH_4$$
$$\text{(b)} \quad CO + 3H_2 = H_2O + CH_4,$$
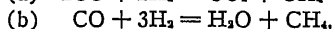
[65] Sabatier, *Compt. rend.* **124**, 1358 (1897); *Ann.* 3447, 34, 360, 418, 435, 477 (1905) *Ann. chim. phys.* (8), **4**, 418 (1905).
[66] a. Mayer and Henseling, *J. Gasbeleucht.* **52**, 166, 194, 242 and 324 (1909); b. Mayer and Jacoby, *ibid.* 305; *compare* Mayer and Altmayer, *ibid.* 238 and 326; *Ber.* **40**, 2134 (1907).
[67] Armstrong and Hilditch, *Proc. Roy Soc.* **103A**, 25-34, 586-97 (1923).
[68] Medsforth, *J. Chem. Soc.* **123**, 1452 (1923).
[69] Emmett, *J. Chem. Ed.* **7**, 2571 (1930).
[70] Chakravarty and Ghosh, *J. Indian Chem. Soc.* **4**, 431-6 (1927).

the latter is favored by high space velocities, i.e., short times of contact, and by the use of ceria as a promoter for nickel. The reduction of carbon monoxide to methane and carbon dioxide, (a), is promoted by vanadium pentoxide at 400° to 500° C. but only very slightly by ceria. Both reactions are exothermic and self-supporting at 500° C. Thoria when used as a promoter for nickel is said to increase its activity seven fold.[71] Neumann and Jacob [72] have observed that porcelain and magnesia impregnated with finely divided nickel are excellent hydrogenating catalysts for carbon monoxide. Yields of 100 per cent methane were obtained at 288° C. and 300° C., respectively, by using 7.4 grams nickel to 37.9 grams porcelain and 6.6 grams nickel to 45 grams magnesia.

Jochum,[73] however, working with various mixtures of carbon monoxide and hydrogen ranging from a composition of 1:1 and 1:5, respectively, found that gas velocity over the nickel catalyst had practically no effect on the composition of the exit gases. With a ratio of carbon monoxide and hydrogen of 1:3 the best operation was obtained at 270° to 280° C., and with a ratio of 1:5 the preferred temperature was 300° to 350° C. Sulfur and aromatic compounds were found to destroy catalyst activity.

Comparative studies [74] which have been made with iron and cobalt catalysts have shown that iron accelerates the reaction leading to the formation of carbon dioxide,

$$2CO + 2H_2 = CH_4 + CO_2$$
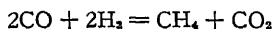
whereas cobalt catalysts have the greater effect toward the reaction giving rise to water,

$$CO + 3H_2 = CH_4 + H_2O.$$
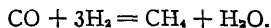
For a given rate of methane formation the iron catalysts required a higher temperature than cobalt. Although iron-copper catalysts led to the formation of only lower hydrocarbons, a catalyst comprising iron-copper-sodium carbonate in the ratio 1:1:0.02 resulted in a yield of 1.8 cc. "kerosene" and 1.4 cc. of "gasoline" from 157 liters of gas. Cobalt-copper catalysts promoted with magnesium oxide or zirconium oxide gave somewhat higher yields of liquid hydrocarbons. Iron catalysts were not promoted by the addition of magnesium oxide.

In connection with the action of iron in promoting methane synthesis, it is to be noted that the observations which have been reported by different investigators vary considerably. For example, Sabatier and Senderens [75] working with the metal in finely divided condition, stated that its efficiency as a catalyst in this reaction is negligible. The results of more recent investigations by Meyer and Henseling,[66a] Armstrong and Hilditch,[67]

[71] *Gas World*, 80, 647-50 (1924).
[72] Neumann and Jacob, *Z. Electrochem.* 30, 557-76 (1924).
[73] Jochum, *J. Gasbeleucht.* 57, 73-80; 103-5; 124-31; 149-51 (1914).
[74] Kodama, *Sci. Papers Inst. Phys. Chem. Research* (*Tokyo*) 14, 169-83 (1930) (in German).
[75] Sabatier and Senderens, *Compt. rend.* 134, 514, 689 (1902).

Fischer, Tropsch and Mehr,[76] Fischer, Tropsch and Dilthey [77] and by Fischer and Tropsch,[78] tend to show that while the activity of the metal in various states of aggregation is slight at ordinary pressures and at temperatures up to 450° C., yields as high as 33.5 per cent methane may, nevertheless, be obtained by operating in the presence of iron filings at 420° C. and a pressure of 20 atmospheres.

A patent issued to the Badische Anilin u. Soda Fabrik [79] contains the statement that concentrations of carbon monoxide to hydrogen in the proportion of 1 to 3.2-4 by volume may be operated successfully at 240° C. in the presence of reduced nickel activated by 1 per cent alumina and supported on pieces of clay. The reaction product containing 84 per cent methane, 15 per cent hydrogen and 1 per cent carbon monoxide may be treated with carbon dioxide and passed a second time over the nickel-alumina catalyst at 270° C. or the excess hydrogen may be removed by oxidation in the presence of free oxygen and a selective catalyst such as cupric oxide or oxides of copper and manganese, for the purpose of furnishing pure methane. An addition [80] to this patent describes the preliminary conversion of carbon monoxide-hydrogen mixtures over an iron oxide catalyst at about 550° C. Final reduction is obtained by passing the gases over active nickel at 240° C. The product consisted principally of carbon dioxide and methane.

The use of finely divided metallic molybdenum, tungsten and other members of this group as catalysts in the reduction of both oxides of carbon at temperatures of 800° to 850° C. has been patented by Schwartzkopf.[81] This process involves the use of an electric furnace lined with platinum, nickel, or platinum-nickel foil. The claim is made that 10 per cent of the reaction gases is transformed into methane in a single passage through the catalyst furnace. The advantage which the above metals are claimed to possess over others applicable to the reaction is their ability to resist the action of various poisons and particularly sulfur compounds.

The behavior of carbon monoxide-hydrogen mixtures in the presence of metals of the platinum group has been made the subject of special study by a number of investigators. Orloff [82] was the first to observe that under certain conditions in the presence of a nickel-palladium catalyst, a reaction took place which resulted in the formation of ethylene. This is in contradiction to the observations of Breteau,[83] who stated that in the presence of palladium sponge, carbon monoxide and hydrogen react in the cold to form methane and that at 400° C. this transformation becomes fairly rapid. Recently it has seemed desirable that the experiments of Orloff

[76] Fischer, Tropsch, and Mehr, *Brennstoff Chem.* 4, 197 (1923).
[77] Fischer, Tropsch and Dilthey, *ibid.* 6, 265-71 (1925).
[78] Fischer and Tropsch, *ibid.* 4, 193-197 (1923); *also* 5, 201-208 (1924).
[79] Ger. Pat. 366,791 (1921) Badische Anilin u. Soda Fabrik; *compare* 303,718 (1914).
[80] Ger. Pat. 390,861 (1922) Badische Anilin u. Soda Fabrik.
[81] Ger. Pat. 362,462 (1921) Schwartzkopf, assr. to Deutsch Glubbaden Fabrik G.M.b.H.
[82] Orloff, *Ber.* 42, 893 (1909).
[83] Breteau, "Etude sur les. meth. d'hydrogenation," 1911, p. 22.

should be repeated. This has now been done and the special precautions under which the experiments were conducted are described in detail by Fester.[84] The results show that under the conditions employed no saturated hydrocarbons are formed. The yield in unsaturated compounds was found to be 4.7 per cent as compared with Orloff's 8.3 per cent. Similar experiments conducted in the presence of palladium asbestos gave 1.5 per cent unsaturated and no saturated hydrocarbons. This work was later extended by Fester,[85] who found that in the presence of nickel-palladium and palladium-carbon catalysts carbon monoxide showed a tendency to resist the reducing action of hydrogen and to undergo decarbonization:

$$2CO = CO_2 + C.$$

This action began at 100° C. in the presence of palladium on active carbon, and at 240° C. about 55 per cent of the carbon monoxide had been decomposed.[86] The percentage of carbon dioxide which was formed was relatively higher if the carbon monoxide was moist, showing that water plays an important rôle in the decomposition of this substance.[87] The absorption of carbon monoxide and hydrogen by palladium on copper has been investigated by Hurst and Rideal [88] and a study of the absorption of platinum surfaces by Langmuir.[89]

In their studies on the formation of methane by the reduction of carbon monoxide by hydrogen, Sabatier and Senderens [75] found that at 250° C. over a nickel catalyst a mixture of 25 carbon monoxide-75 hydrogen by volume gave almost pure methane. At 380° C. the gaseous product had the composition: CO_2, 10 per cent; CH_4, 67.9 per cent; H_2, 21.6 per cent. However, when a mixture of equal volumes of hydrogen and carbon monoxide was used at 380° C., the volume of carbon dioxide produced was greater than that of the methane as shown by the composition of the product:

CO_2, 52.5 per cent; CH_4, 39.8 per cent; H_2, 7.1 per cent; CO, 0.6 per cent.

Of the two routes by which carbon monoxide may be reduced by hydrogen:

(a) $2CO + 2H_2 = CH_4 + CO_2$
(b) $CO + 3H_2 = CH_4 + H_2O$
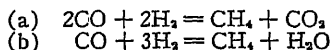
the former has the greater thermodynamic tendency to take place. Thus, according to the calculations of Smith [90] the equilibrium constants for the two reactions are as shown in Table III.

[84] Fester, *Brennstoff Chem.* 3, 244 (1922).
[85] Fester, *Brennstoff Chem.* 5, 49-53 (1924).
[86] a. *Compare* Sabatier and Senderens, *Bull. soc. chim.* (3) 29, 294 (1903); b. Mayer, Henseling and Altmayer, *J. Gasbeleucht.* 52, 166 (1909).
[87] *Compare* a. Wieland, *Ber.* 45, 679 (1912); b. Bancroft, *Trans. Am. Electrochem Soc.* 32, 439 (1917); c. Taylor, *J. Ind. Eng. Chem.* 13, 75 (1921); *J. Am. Chem. Soc.* 43, 1273 (1921); d. Rideal, *J. Chem. Soc.* 115, 993 (1919).
[88] Hurst and Rideal, *J. Chem. Soc.* 125, 694-705 (1924).
[89] Langmuir, *J. Am. Chem. Soc.* 40, 1361 (1918).
[90] Smith, *Ind. Eng. Chem.* 19, 801-3 (1927).

TABLE III.—*Methane by the Reduction of Carbon Monoxide by Hydrogen.*

Reaction	(a)	(b)
K at 25° C.	1.9×10^{30}	1.4×10^{25}
K at 300° C.	5.6×10^{8}	1.5×10^{7}
K at 400° C.	1.7×10^{5}	1.6×10^{4}

It has been shown experimentally [91] that with a 1:1 mixture of carbon monoxide and hydrogen passed over a supported nickel catalyst at 290° to 340° C., 80 per cent of the carbon monoxide reacted to form methane by equation (a) and only 20 per cent by equation (b). No carbon was deposited in this temperature range and a time of contact of 10 seconds gave the maximum conversion. Very little reaction occurred below 290° C. Increasing space velocity favored reaction (b) in the presence of sugar charcoal-pumice-vanadium pentoxide-nickel catalysts although even with a space velocity of 1500 volumes of gas per volume of catalyst per hour only 20 per cent of the methane was formed by reaction (b).[70]

Neumann and Jacob,[72] on the other hand, found very small amounts of carbon dioxide formed even at 450° C. This difference in results is largely due to difference in composition of the gas mixture used for the synthesis. When hydrogen is present in greater proportion than is called for by the theoretical 1:3 ratio for reaction (b), as was the case with Neumann and Jacob's work, reaction (b) tends to predominate and when the ratio is nearer 1:1, carbon monoxide to hydrogen, reaction (a) predominates.

Also, when water vapor is present in considerable amounts, the overall reaction:

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$
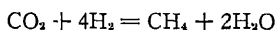
is inhibited and the reaction:

$$2CO + 2H_2 = CH_4 + CO_2$$

predominates.[92] In cases where the water vapor was allowed to build up in concentration or was present in considerable quantities from the start, the carbon monoxide content of the exit gases dropped to very low values of less than 3 per cent and the carbon dioxide concentration increased to almost 40 per cent (wet basis). However, when a 1:1 initial mixture was recirculated over the catalyst with water removal between passes, the carbon monoxide remained high and the carbon dioxide low. The fact that the water gas catalytic reaction:

$$CO + H_2O = H_2 + CO_2$$
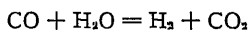
prevails in so many different systems and in the presence of such a variety of catalysts, as have been found to affect it, leads to the assumption that it does not require a very specific catalyst and may often unsuspectedly alter the results. At temperatures up to 500° C. equilibrium of this reac-

[91] Haslam and Forrest, *Gas Age Record*, **52**, 615 (1923).
[92] Hightower and White, *Ind. Eng. Chem.* **20**, 10-15 (1928).

tion is in favor of carbon dioxide formation even when somewhat less than the theoretical amount of steam is present.

This superposition of two limited reactions is shown in the results of experiments by Pascal and Botolfsen.[93] A mixture of carbon monoxide and water vapor was passed over a nickel carbonate catalyst, prepared from nickel nitrate by precipitation with magnesium carbonate and "forming" by heating to 700° C. Reaction was observed to begin at 250° C. and to yield methane quantitatively up to 275° C. Above this temperature the second reaction leading to the formation of carbon dioxide and hydrogen was the more prominent. At 750° C. the formation of methane no longer occurred and the formation of hydrogen was predominant.

Reduction of Carbon Dioxide by Hydrogen to Form Methane

The reduction of carbon dioxide by hydrogen in the presence of metal catalysts active toward hydrogenation has been the subject of investigations by Jahn[94] and Bach,[95] both of whom were particularly interested in the accelerating effect of palladium. Activation by finely divided nickel was studied somewhat later by Sabatier and Senderens,[75] who stated that hydrogenation begins at 230° C. and is complete at 300° C. It is to be noted that both of these temperatures are higher than the corresponding temperatures for the hydrogenation of carbon monoxide. When the reaction is carried on between 300° and 400° C. under conditions such that hydrogen is always present in slight excess of the amounts required by the equation, excellent yields of methane may be obtained.[96]

$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$
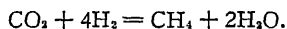
If hydrogen is present in slight excess, i.e., 80 per cent or more, hydrogen in the mixture, then the carbon dioxide is almost completely reduced at 300° C. and methane of high purity is produced.

The results of Hightower and White's work[92] confirm those of the earlier workers. With a nickel catalyst prepared by the decomposition of nickel nitrate on porcelain in a current of hydrogen, these workers obtained the following results from single slow passes of the gas mixture over the catalyst at 350° C.:

TABLE IV.—*Reduction of Carbon Dioxide at 350° C. Over Nickel.*

Gas	Initial	Final	Initial	Final
		Per Cent		
H_2O	3.0	47.5	8.4	44.3
CO_2	18.8	4.4	21.5	11.1
CO	0	0.1	0	0.2
CH_4	0	25.9	0	20.3
H_2	76.4	19.7	68.7	22.1
N_2	1.4	2.1	1.6	1.8

[93] Pascal and Botolfsen, *Compt. rend.* 191, 186-7 (1930).
[94] Jahn, *Ber.* 22, 989 (1889).
[95] Bach, *Compt. rend.* 116, 1389 (1893).
[96] Fr. Patent, 356,471 (1905) Sabatier.

The overall reaction apparently proceeded without complications:

$$CO_2 + 4H_2 = CH_4 + 2H_2O.$$
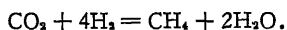
The action of cobalt is considerably less vigorous than that of nickel. Carbon dioxide is reduced by hydrogen to methane over cobalt catalysts to a slight extent at 300° C. and rather rapidly at temperatures near 400° C. Although equilibrium is in favor of hydrogen and carbon dioxide at low temperatures in the catalytic water gas reaction:

$$CO_2 + H_2 = CO + H_2O,$$
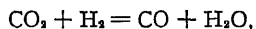
some reduction of carbon dioxide may occur at low temperatures. Bahr [97] noticed reaction at 200° C. in the presence of copper. With catalysts of copper chromate, iron-copper, iron-cobalt, and cobalt-copper-zinc and at temperatures between 200° and 450° C. quantities of carbon monoxide up to 16 per cent were obtained with mixtures of carbon dioxide and hydrogen in the ratios 1:1 and 1:3. At slow gas flows, i.e., long times of contact, reduction to methane occurred, especially with catalysts containing cobalt.

The catalytic effect of iron is shown by the results obtained from a mixture of 15 per cent carbon dioxide, 23 per cent carbon monoxide, and 56 per cent hydrogen. When this mixture at a pressure of 120 to 150 atmospheres was brought into contact with a red hot spiral of iron wire a gas mixture containing 9 per cent carbon dioxide, 40 per cent carbon monoxide, 22 to 29 per cent hydrogen, and 15 to 19 per cent methane was formed.[98] Considerable carbon was deposited on the spiral. At a spiral temperature of about 600° C. the hydrogen was practically all consumed but considerable free carbon was still deposited. Activation of the iron wire with alkali did not alter the action except to decrease the yields of formaldehyde that had been obtained.

Although the reduction of carbon dioxide has usually been considered in connection with all reactions involving the hydrogenation of carbon monoxide, particular references may be made at this point to the work of Ipatiew,[15] Mayer and Henseling,[66a] Neumann and Jacob,[72] and Taylor and Burns.[87c]

Relatively little work has been done with carbon dioxide reduction for the formation of methane, however, because of the waste of hydrogen involved when the process is considered from an economic standpoint. Promoter action of thoria on nickel has been studied by Taylor and Russell,[99] the interaction of hydrogen and carbon dioxide on the surfaces of platinum and tungsten by Prichard and Hinshelwood,[100] and the formation of formaldehyde by the action of carbon dioxide, hydrogen and

[97] Bahr, *Ges. Abhandl. Kenntnis Kohle* 8, 219-24 (1930). *Chem. Zentr.* 1930, I, 185-6.
[98] Fischer and Jaeger, *Ges. Abhandl. Kenntnis. Kohle* 7, 68-74 (1925).
[99] Taylor and Russell, *J. Phys. Chem.* 29, 1325-41 (1925).
[100] Prichard and Hinshelwood, *J. Chem. Soc.* 127, 806-811, 1546 (1925).

steam at 240° to 250° C. in the presence of contact substances provided with a metallic deposit of copper, nickel and the like, by Heinemann.[101]

Synthesis of Hydrocarbons Higher Than Methane

Carbon monoxide reduced by hydrogen at low temperatures (100° C.) in the presence of active nickel or palladium catalysts mounted on asbestos, tends to form unsaturated hydrocarbons.[102] The catalysts soon lose activity and relatively low yields are obtained.[103]

Somewhat later than Orloff's early experiments on the synthesis of hydrocarbons from water-gas mixtures, the Badische Company in Germany attempted the synthesis of organic compounds from water-gas [104] Mixtures containing excess carbon monoxide were passed over catalysts composed of members of the iron group of the periodic system or their oxides at pressures up to 120 atmospheres and temperatures of about 400° C. Oils composed largely of hydrocarbons and consisting of about 2/3 saturated and 1/3 unsaturated molecules were formed. Some oxygen-containing compounds were also found in the products. Catalysts of cobalt oxide promoted with osmium oxide were found to give rise to the formation of mixtures of liquid hydrocarbons together with oxygenated derivatives when hydrogen-carbon monoxide mixtures were treated at 300° to 400° C. and 100 atmospheres pressure.[105]

With catalysts of iron or cobalt, variously supported, and formed by reduction of the oxides with hydrogen at 350° C., Fischer and Tropsch [106] were able to obtain the higher homologs of methane from mixtures of carbon monoxide and hydrogen at temperatures ranging from 250° to 300° C. The products contained proportions of ethane, propane, butane, and higher members up to solid wax.[107] Olefins were present to only a very small extent. Since a wide range of mixtures and rates were used in obtaining the higher hydrocarbons, it seems probable that the catalysts used were responsible for the change in product from methane, as had been obtained in the presence of nickel catalysts, to the higher homologs.

With certain catalysts such as zinc oxide and finely divided iron it was found that the temperature at which reaction was made to occur was the controlling factor in determining the character of the product.[108] Thus, with the zinc oxide catalyst only methane was obtained at 480° C., a mixture of 80 per cent methane and 20 per cent higher homologs at 380° C., and a mixture of 10 per cent methane and 90 per cent higher homologs at 300° C. This is not true of nickel catalysts as the hydrogenating activ-

[101] U.S. Pat. 1,460,244 (1922) Heinemann; *compare Compt. rend.* **150,** 1568 (1910) and **151,** 358 (1910).
[102] Orloff, *J. Russ. Phys. Chem. Soc.* **40,** 1588 (1908).
[103] *See also* Fester, *Brennstoff Chem.* **3,** 224 (1922).
[104] Brit. Pat. 20.488 (1913) Badische Anilin u. Soda Fabrik.
[105] Ger. Pat. 293,787 (1916) Badische Anilin u. Soda Fabrik.
[106] Fischer and Tropsch, *Brennstoff Chem.* **7,** 97-104 (1926); *Ber.* **59B,** 830-1, 832-6 (1926).
[107] Fischer and Tropsch, *Ber.* **59,** 923 (1926).
[108] Brit. Pat. 255,818 (1925) Fischer and Tropsch.

ity is so intense in this case that only methane is obtainable under normal conditions.

With a catalyst of cobalt-manganese oxide-copper small yields of higher hydrocarbons have been obtained together with oxygenated products.[100] The synthesis of identifiable quantities of olefin hydrocarbons were reported in 1927.[110]

Because of the possible importance of the process for the production of a liquid motor fuel from coal and the possible bearing it might have on the synthesis of oxygenated products from water-gas, a considerable amount of research has been expended on the problem both in this country and abroad.[111] The reverse reactions, however, are of limited importance since at the temperatures required, the aliphatic hydrocarbons higher than methane undergo decomposition reactions in the presence of the active catalysts.

Various mechanisms have been proposed for the formation of the higher hydrocarbons. Elvins and Nash [100a] suggested, as the result of their findings of oxygenated compounds in their product, that the formation of oxygen-containing compounds represents the first step in the process and that the higher members were built from these. Fischer and Tropsch [111b] suggested the possibility that methylene (CH_2) was formed by the action of hydrogen on carbides at the catalyst surface and then rapidly polymerized to higher hydrocarbons. The fact that passage of hydrogen over metallic carbides does not result in the formation of higher hydrocarbons does not necessarily disprove this theory since the carbides at the catalyst surface are supposed to lead a highly active and transitory life, and might be present at a catalyst surface with a higher energy content. The suggestion that higher hydrocarbons may form as a primary action is improbable because of the large number of molecules necessarily involved in such a case. Smith, Hawk, and Golden [112] regard olefins as the primary products which may be later hydrogenated, reacted with carbon monoxide, dehydrated, polymerized, or otherwise reacted upon to form the higher hydrocarbons. The mechanism for the formation of the primary olefin product is suggested to be through the association of hydrogen and carbon monoxide at the catalyst surface followed by a decompo-

[100] a. Elvins and Nash, *Fuel* 5, 263 (1926); *Nature* 118, 154 (1926); b. Fischer and Tropsch, *Brennstoff Chem.* 7, 299 (1926).
[110] Smith, Davis and Reynolds, *Am. Chem. Soc.* Meeting September 1927; *Ind. Eng. Chem.* 20, 462 (1928).
[111] *See also:* a. Elvins, *J. Soc. Chem. Ind.* 46, 473T (1927). b. Fischer and Tropsch, *Brennstoff Chem.* 9, 21 (1928). c. Smith, Hawk and Reynolds, *Ind. Eng. Chem.* 20, 1341 (1928). d. Tropsch and Koch, *Brennstoff Chem.* 10, 337 (1929). e. Audibert, *Fuel Sci. Pract.* 5, 170-7 (1926). f. Nash, *J. Soc. Chem. Ind* 45, 876-8 (1926). g. Fischer, *Internl. Conf. Bit. Coal.* 1926, 234-46. h. Fischer, Tropsch, and Ter-Nedden, *Ber.* 60B, 1330-4 (1927). i. Fischer, *Brennstoff Chem.* 8, 1-5 (1927). j. Fischer and Tropsch, *Brennstoff Chem.* 8, 165-7 (1927). k. Tropsch, *Brennstoff Chem.* 8, 376 (1927). l. Fischer, *Natl. Petroleum News* 18, No. 47, 49-51 (1926). m. Brit. Pat. 271,452 (1926) I. G. Farbenind. n. Smith, *Ind Eng. Chem.* 20, 859-60 (1928). o. Erdley and Nash, *J. Soc. Chem. Ind.* 47, 219-23T (1928). p. Berl and Jungling, *Z. angew. Chem.* 43, 435-40 (1930). q. Brit. Pat. 291,867 (1927) Nash, Bowen, and Elvins. r. Brit. Pat. 293,185 (1927) I. G. Farbenind. s. Brit. Pat. 310,999 (1928) I. G. Farbenind. t. Fischer, "The Conversion of Coal into Oils," English Ed. by Lessing, New York (1925), D. Van Nostrand Co. Inc., 1925.
[112] Smith, Hawk, and Golden, *J. Am. Chem. Soc.* 52, 3221-32 (1930).

sition to olefin and water. This mechanism was experimentally found to occur over a cobalt-copper-manganese oxide catalyst but not over an iron-copper catalyst.

Thermodynamical calculations [90] have shown that it becomes increasingly easier to form the higher hydrocarbons than the lower members, from mixtures of hydrogen and carbon monoxide. This is shown in the case of the following reactions by the values of the equilibrium constant at several different temperatures. Because of the large volume decrease occurring in these reactions,

$$
\begin{array}{ll}
\text{a.} & 2CO + 5H_2 \rightleftarrows C_2H_6 + 2H_2O(g) \\
\text{b.} & 4CO + 3H_2 \rightleftarrows C_2H_6 + 2CO_2 \\
\text{c.} & 3CO + 7H_2 \rightleftarrows C_3H_8 + 3H_2O(g) \\
\text{d.} & 6CO + 4H_2 \rightleftarrows C_3H_8 + 3CO_2 \\
\text{e.} & 6CO + 9H_2 \rightleftarrows C_6H_6(g) + 6H_2O(g) \\
\text{f.} & 12CO + 3H_2 \rightleftarrows C_6H_6(g) + 6CO_2
\end{array}
$$
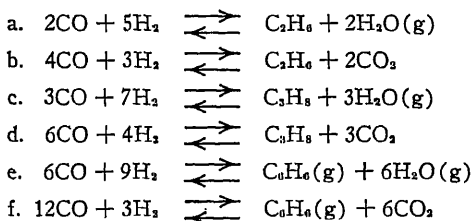
TABLE V.—*Higher Hydrocarbons by the Reduction of Carbon Monoxide by Hydrogen.*

Product	Ethane		Propane		Benzene	
Reaction	a	b	c	d	e	f
K at 25° C.	2.4×10^{40}	4.8×10^{50}	2.0×10^{56}	5.6×10^{71}	7.7×10^{76}	6.0×10^{107}
K at 300° C.	1.9×10^{9}	2.7×10^{13}	3.2×10^{13}	1.7×10^{17}	9.5×10^{15}	2.5×10^{25}
K at 400° C.	1.3×10^{4}	1.3×10^{6}	1.7×10^{5}	1.8×10^{8}	8.1×10^{5}	9.9×10^{11}

increase of pressure greatly favors the formation of the products and conversely, decrease of pressure favors decomposition.

Experimentally increased pressures or decreased temperatures have been found to favor the formation of higher hydrocarbons. Also the shorter the time of contact at any given condition the higher will be the proportion of hydrocarbons higher than methane. Thus, with a nickel catalyst the temperature should be about 160° C. for best results, with cobalt about 270° C., and with iron about 300° C.[100] Yields of 190 grams of the higher hydrocarbons per cubic meter of water-gas have been reported.

However, as the pressure is increased above about 10 to 15 atmospheres, especially when metallic oxide catalysts or metal-alkali catalysts are used, the product tends to become more and more oxygenated in character and exceedingly complex mixtures may be obtained. Such products, because of their complexity and difficulty of separation into components, are of little commercial value from the standpoint of being sources of valuable oxygenated organic compounds.

Francis' calculations [118] have shown that per volume of water-gas reacted, considering hydrogen and carbon monoxide as equivalent, the formation of carbon dioxide is accompanied by the largest free energy

[118] Francis, *Proc. 10th Annual Meeting Am. Petroleum Inst.* **III**, 97 (1930).

decrease, and of water by the next largest decrease. Of the hydrocarbons, methane is formed with the largest free energy decrease per volume of water-gas reacted. Methanol formation is accompanied by the smallest decrease. However, the formation of methanol is accompanied by a larger decrease in volume than the formation of hydrocarbons from water-gas, so that pressure may be used to direct the reaction to methanol as is done industrially today in the presence of mixed oxide type catalysts. Although the most pronounced effect of pressure in changing the character of the product from hydrocarbons to oxygen containing compounds may be due to a shift in the equilibrium concentrations of the components, it is possible that changes in specific reaction rates of the various reactions involved may be accountable.

Synthesis of Methanol and of Mixtures of Oxygenated Compounds

Although it is now possible to synthesize pure methanol from mixtures of hydrogen and carbon monoxide under pressure and in the presence of extremely selective catalysts, the process is relatively new and a large amount of research was necessary before it could be brought to the industrial stage. Among the results of this early work much valuable information on catalytic action is to be found.

The catalysts which were found to be effective in the formation of methane from hydrogen and carbon monoxide with the greatest activity were composed of nickel, iron, cobalt, and molybdenum. The catalysts most active in methanol synthesis in general consists of the oxides or mixtures of the oxides of zinc, copper, or chromium. Iron promoted with alkali has been found to be very active but not at all directive in the synthesis of aliphatic compounds from water-gas. With it only a very complex mixture results, which it is impossible to separate commercially into constituents.

Synthesis of Mixtures of Oxygenated Compounds

The first evidences that oxygenated compounds had been formed from water-gas in the presence of catalysts and under high pressure are to be found in the patents to the Badische Anilin u. Soda Fabrik.[114] A product comprising a mixture of aliphatic hydrocarbons, alcohols, and other oxygen containing organic compounds was claimed. The catalysts consisted of metallic oxides or mixtures of oxides of such metals as zinc and cobalt promoted with an alkali metal carbonate or hydroxide. Later, catalysts resistant to sulfur poisoning, such as mixtures of the sulfides of zinc, copper, lead, or cadmium with chromium oxide were patented.[115]

[114] Ger. Pat. 293,787 (March 8, 1913); 295,202-3 (1914); Fr. Pat. 468-427 (1914); Brit. Pat. 20,488 (1915) Badische Anilin u. Soda Fabrik; and U.S. Pat. 1,201,850 (1916) Mittasch and Schneider.
[115] *See* French Pat. 689,342 (1930) Dreyfus.

The effect of these patents was to stimulate research on the pressure synthesis of organic compounds from water-gas. As a consequence much controversy and confusion arose in regard to the efficacy of the different catalysts, due largely to the use of a diversity of experimental conditions by the several investigators.

Among the early researches on the synthesis of organic compounds from water-gas were those of Fischer, Tropsch and their collaborators on the formation of "synthol" and its derived product "synthin." These names have been applied to the complex mixtures which result from the interaction of hydrogen and carbon monoxide under moderate pressure in the presence of a catalyst which consists of mixtures of (1) hydrogenating-dehydrogenating metals such as iron, nickel, etc., and (2) hydrating-dehydrating oxides such as oxides of the alkali and alkali earth metals, etc. The products obtained at pressures of 10 to 15 atmospheres are distinctly intermediate in character, being neither exclusively hydrocarbons as in the case of atmospheric pressure synthesis nor mainly oxygenated compounds as in the high pressure synthesis. The exact nature of the mixtures which are formed vary with the temperature and pressure conditions of operation but in general consist of homologous aliphatic alcohols, aldehydes, and acids containing from one to eight carbon atoms together with corresponding ethers, esters, and ketones.[110] This mixture which is known as "synthol" and which is almost completely soluble in water undergoes a gradual change in its composition when heated for several hours under pressure and passes over into "synthin." The latter is characterized by the fact that it contains a high percentage of mixed liquid hydrocarbons having a consistency similar to gasoline, and is insoluble in water. This first product is of interest because of the fact that it is suitable for commercial application as a substitute for gasoline.

It seems probable that the development of Fischer's synthesis arose from his attempts to duplicate the results claimed with the zinc oxide-alkali catalysts in the Badische Anilin u. Soda Fabrik patents. Fischer[111] concluded that a hydrogenating catalyst such as iron was essential to reaction. In some of his early work Vignon had obtained high yields of methane from water-gas by the use of iron filings as a catalyst.[4a] He was also able to demonstrate the efficiency of calcium oxide as a catalyst for this reaction. The mechanism of the latter process was interpreted by assuming the intermediate formation of calcium formate. In repeating these experiments Tropsch[117] was unable to duplicate the results described by Vignon in the case of either the iron or the lime catalyst, but, nevertheless, obtained data which led him to consider that a continuation of both lines of investigation with a view to determining the specific action of each of these catalysts on the water-gas system was greatly to be desired.

[110] a. Fischer and Tropsch, *Ber.* **56**, 2431-6 (1923); b. Fischer and Tropsch, *Brennstoff Chem.* **8**, 165-7 (1927).
[117] Tropsch, and Schelling, *Brennstoff. Chem.* **3**, 33 (1922).

Tropsch expanded the investigations of calcium oxide as a catalyst for reactions in water-gas mixtures and included a study of the synthesis and decomposition of formates.[118] In explaining the mechanism of methane synthesis Vignon assumed that at temperatures below the decomposition of calcium carbonate (900° C.) water-gas reacts with calcium oxide to give calcium formate.

$$CaO + 2CO + H_2O = Ca(CHO_2)_2.$$

The formate in the presence of an excess of lime was then supposed to react to give methane and calcium carbonate according to the equation:

$$2Ca(HCO_2)_2 + CaO = 3CaCO_3 + CH_4.$$
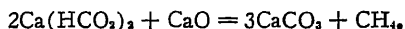
This explanation of hydrocarbon formation was based on the observation [119] that when heated alone at temperatures of 360° to 370° C. calcium formate decomposed to yield small quantities of hydrocarbons together with other products. The experiments of Fischer and Tropsch demonstrated that at temperatures of 420° to 430° C. calcium formate decomposes to give, in addition to calcium carbonate and a small quantity of calcium oxalate, a complicated mixture of gaseous and liquid products. The gases consist of carbon dioxide, carbon monoxide, hydrogen and hydrocarbons including methane. The liquids correspond to two fractions: (a) described as a light inflammable liquid consisting of water, methyl alcohol, acetone, formic acid and other fatty acids, and (b) described as dark oily drops. Large excess of calcium oxide served to decrease the yield of liquids and to increase the yield of gaseous products. Treatment of calcium formate with steam under pressure gave a yield of methanol equal to about 52 per cent of theory and left a residue of pure white calcium carbonate. A study of the decomposition of the formates of barium, magnesium, and lithium showed a close resemblance between these and the calcium salt with certain variations in the relative quantities of the decomposition products at different temperatures.[120]

The synthesis and decomposition of formates has been the subject of a number of other investigations and it has long been known that the formates of different metals decompose differently and that even one and the same formate may be made to yield a variety of products under different conditions. The salts of the alkaline earth metals have in particular found application in organic chemistry in connection with the preparation of formaldehyde and its higher homologs. Systematic research in this field has been attempted by Bredig and Carter [121] and by Hofmann in collaboration with others.[122] The former investigators were

[118] Tropsch, *Ann. chim. phys.* (9) 15, 42-60 (1921).
[119] Fischer, Tropsch, and Schellenberg, *Abhandl. Kohle* 6, 330 (1921).
[120] Fischer and Tropsch, *Abhandl. Kohle* 6, 355 (1921).
[121] Bredig and Carter, *Ber.* 47, 541-45 (1914).
[122] a. Hofmann and Helge, *Ber.* 51, 1389-98 (1918); b. Hofmann and Schibsted, *Ber.* 51, 1398-1418 (1918).

able to show that hydrogen at high pressures and in the presence of a platinum or palladium catalyst reacts with bicarbonates to give formates and that the same product may be obtained from carbonates or the calcium salts of other weak acids if carbon dioxide is mixed with the hydrogen. In the case of calcium salts, 100 per cent yields of formate were obtained in four hours at 50 atmospheres, while in the case of potassium bicarbonate at the same temperature (70° C.) about 74 per cent yields were obtained in 26 hours with hydrogen under a pressure of 60 atmospheres. Hofmann undertook a systematic study of the action of heat upon a large number of metallic formates and found that the temperature at which decomposition begins increases regularly with an increase in the basic properties of the metal, viz: the formate of copper begins to decompose at 170° C., of lead at 195° to 200° C., of nickel at 210° C., of zinc at 240° C., of iron at 245° C., of manganese at 295° C., of barium at 325° C., of calcium at 335° C., of magnesium at 340° C., of strontium at 355° C., of sodium at 355° C. At different temperatures above the initial decomposition temperature a given formate may decompose in any of several ways. For example, at temperatures between 400° and 500° C. lithium formate may be made to yield methanol, acetone, formic acid, carbon dioxide and water in varying amounts. Magnesium formate when heated above 340° C. yields methanol, acetone and formaldehyde. Copper and nickel salts tend to favor the formation of methanol. Zinc formate gives particularly good yields of formaldehyde and methanol. Lead and chromium salts produce the same mixture. Tin formate gives formaldehyde but no methanol and aluminum formate gives neither formaldehyde nor methanol. In conclusion the authors state that it is possible to apply these facts to transformation of formic acid in the vapor phase in the presence of chemically unchanged catalysts if the catalyst and temperature are so chosen as to allow of the possibility of formate formation. Under these circumstances cyclic processes involving the synthesis and decomposition of formates may be adapted to the preparation of methanol and of formaldehyde. The best catalysts for the preparation of aldehyde were found to be, zinc oxide or thoria deposited on asbestos. Such a process has been patented.[123] Lithium formate is prepared from the hydroxide and carbon monoxide at 160° to 170° C. and a pressure of 20 to 30 atmospheres. The formate is then decomposed at 350° to 500° C. and the residue of carbonate is transformed directly into formate again. This can be done by treating the mixture with water and heating at 120° to 250° C. in the presence of carbon monoxide under pressure, the resulting gas mixture being freed from any carbon dioxide which is given off during the reaction by washing with water under pressure. The transformation of carbonate to formate is complete when the issuing gases contain no more carbon dioxide. The most favorable temperatures for the decomposition are 380° to 405° C.

[123] Brit. Pat. 173,097 (1921) Badische Anilin u. Soda Fabrik.

Having demonstrated the efficiency of iron as a hydrogenating catalyst and of the alkali and alkali earth metals (in the form of their oxides, hydroxides, carbonates or salts of other weak acids), as hydrating catalysts in reactions involving the reduction and hydrolysis of the oxides of carbon at relatively high temperatures and pressures, Fischer, Tropsch and their collaborators [124] then undertook a large number of comparative experiments with a view to determining the exact effect of different combined catalysts on alcohol formation. In the course of this experimentation the action of a large number of metals, notably iron, nickel, cobalt, and manganese, was investigated in the presence of different promoters such as alumina and compounds of practically all of the alkali and alkali earth metals. The results of these experiments demonstrated [125] that for the synthesis of alcohols it was necessary to have present in the form of a catalyst, a hydrogenating metal such as iron filings and an alkali metal present in fairly large quantities in the form of either the hydroxide or the carbonate. Pressures of at least 75 atmospheres were necessary at a temperature of about 410° C. The relative ratio of hydrogen to carbon monoxide was found distinctly to affect the character of the reaction, an excess of hydrogen being favorable.

The literature is not free from controversy on the subject of the iron-alkali catalysts, however. Audibert and Raineau [126] claim that ferric oxide and not iron is the active catalyst for the formation of liquid products. It has been reported that iron oxide promoted with potassium hydroxide is not active as a catalyst toward this type of reaction.[127] Whether these discrepancies are due to differences in methods and materials of catalyst preparation, differences in methods of operation, or in difference in gas mixtures it is difficult to say although it would seem probable that the trouble lies in the catalyst.

Fischer's experiments with iron catalysts promoted with alkalies showed that they increased in efficiency with the strength of the base, with the exception of caesium. Working with catalysts prepared by calcining steel turnings with potassium hydroxide, Frolich and Lewis [127] showed that with a gas containing 40 per cent carbon monoxide passed into the reactor at a space velocity of 1250 at 200 atmospheres and 325° to 335° C. the best yields were obtained when the base comprised 2.2 per cent of the catalysts (calculated as K_2O). From this it appears that a strong base present in small amount with iron as the catalyst enables the best yields of liquid products to be obtained. This conclusion has been confirmed by the work of Audibert and Raineau.

The effect of pressure on the several reactions possible in the synthesis of organic liquid compounds from water-gas mixtures is shown by the change in character of the product from one predominately hydrocarbon

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[124] a. Fischer, Tropsch and Dilthey, *Brennstoff Chem.* **6**, 265-71 (1925); b. Fischer and Tropsch, *Ber.* **56**, 2428-43 (1923).
[125] Fischer and Tropsch, *Brennstoff Chem.* **5**, 201-208 (1924).
[126] Audibert and Raineau, *Ind. Eng. Chem.* **21**, 880 (1929).
[127] Frolich and Lewis, *Ind. Eng. Chem.* **20**, 354 (1928).

in nature formed at atmospheric pressure to one predominately oxygenated in character at pressures above 100 atmospheres pressure.[110b] The reason for this change is to be found partly in the character of the adsorption of the reactants at the catalyst surface and partly in the effect of pressure in shifting the equilibrium in favor of the product formed with the greatest decrease in gas volume. The methane reaction:

$$2H_2 + 2CO = CH_4 + CO_2$$
$$3H_2 + CO = CH_4 + H_2O$$
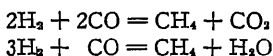
occurs with a decrease in volume of 2 to 1, and is favorably affected by pressure. This points to the necessity in the synthesis of oxygenated compounds for having catalysts more directive in character than in the methane synthesis. The use of iron or iron-copper catalysts, with much less pronounced hydrogenating powers than nickel, and activated or modified with a strong alkali like potassium oxide, was necessary before it was possible to obtain products other than hydrocarbons even under pressure.

Fischer's work has shown that with the iron-alkali type of catalyst the character of the product may be altered by changes in the composition of the water-gas mixture. The early results have been largely confirmed by subsequent workers with similar catalysts. It was found that as the ratio of carbon monoxide to hydrogen was increased the proportion of oily or water insoluble product increased at the expense of the water and water-soluble organic compounds. It has been shown that the water layer of the product may be eliminated entirely by the use of high proportions of carbon monoxide. There is a tendency, however, for the iron catalyst to promote the reaction,

$$2CO = C + CO_2$$
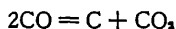
whenever high ratios of carbon monoxide are used. This deposition of carbon fouls the catalyst and alters its activity. The presence of the high boiling materials which form, particularly at the longer times of contact, tend to decrease catalyst activity by depositing on the surface. This is especially true at the high $CO:H_2$ ratios. Even in the presence of a copper-base catalyst Audibert[128] found that mixtures of $CO + H_2$ caused fouling but that mixtures of $CO + 5H_2$ led to the formation of unappreciable traces of tars on the catalyst.

The experimental results have shown that, in general, the yield of oily material increases with increased time of contact of reactants with the catalyst. This fact indicates a stepwise mechanism for the synthesis of the high molecular weight compounds that are obtained. The mechanism proposed by Fischer involved the addition of carbon monoxide to methanol, which formed first, to yield acetic acid which was subsequently reduced

[128] Audibert, *2nd. Internl. Conf. Bit. Coal*, Pittsburgh, **II**, 509 (1928).

by hydrogen to acetaldehyde. By the continued alternate addition of carbon monoxide and reduction by hydrogen, successively higher molecular weight substances were built up.[129] Decomposition of the acids to ketones, condensation of the aldehydes to esters, reduction of the alcohols by carbon monoxide to hydrocarbons, dehydration of the alcohols to olefins—all were reactions possible involved in the process and thermodynamically sound under the conditions.*

Synthesis of Methanol

From the point of view of the utilization of methanol in the production of formaldehyde by oxidation and in other processes in which methanol is subjected to the action of catalysts at elevated temperatures, it is of more importance to consider the equilibria, the mechanism, and the catalysis of the synthesis from water-gas than to consider the more industrial aspects of the process. Hence, no attempt will be made here to picture completely the various commercial aspects of methanol synthesis.

Equilibrium

Although the methanol equilibrium has been the subject of extensive investigation, striking discrepancies still exist in the values which have been obtained. The problem of determining the equilibrium either as a function of temperature or at a single temperature has been attacked by three general methods:

(1) Calculation of the equilibrium constant, K_p, by use of the Nernst approximation formula or by the third law of thermodynamics.

(2) Experimental determination of K_p by indirect methods involving such reactions as,

$$2H_2 + CH_3COOH = 2CH_3OH \qquad (1)$$
$$CH_3OH + CO = CH_3COOH \qquad (2)$$

or

$$H_2 + CO = H_2CO \qquad (3)$$
$$H_2CO + H_2 = CH_3OH \qquad (4)$$
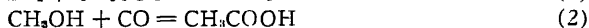
(3) Experimental determination of K_p by direct measurement on the reaction:

$$2H_2 + CO = CH_3OH \qquad (5)$$

at atmospheric and elevated pressures.

The results of various investigators have been collected in tabular form by Wettberg and Dodge [130] and it is from this that Table VI has been devised.

[129] Fischer, *Ind. Eng. Chem.* 17, 576 (1925).
[130] Wettberg and Dodge, *Ind. Eng. Chem.* 22, 1042 (1930).
* *See also* Chapter II, page 38, *et seq.*

TABLE VI.—*Values of K_p Obtained for Methanol Synthesis.*

Pressure atms.	$K_p \times 10^3$ 250° C.	$K_p \times 10^4$ 300° C.	$K_p \times 10^5$ 350° C.	$K_p \times 10^6$ 400° C.	Method of Determining [131]
—	74	81	140	280	Calculated by third law[a]
—	1300	800	1200	2500	Calculated by third law[b]
—	1300	1400	2200	4500	Calculated by third law[c]
1.0	320	430			Indirect method using equations (3) and (4). K_p calculated from results[d]
1.0	4.7	6.0			Indirect method using equations (1) and (2)[e]
1.0	3.1	4.5			Indirect method using equations (1) and (2)[f]
50	1.25	1.90			Direct method. Equil. approached from both sides[f]
1.0	5.90	6.40	7.90	20	Direct method. Equil. approached from both sides[g]
70–100	2.1	1.6	2.0	3.1	Same[h]
204				18.0	Direct method from synthesis side only[i]
150				19.2	Direct method from synthesis side only[j]
180				19.8	Direct method from synthesis side only[k]

	$K_p \times 10^4$ 304° C.	
—	7.4	Calculated from new thermal data[l]
1	4.14	Direct method reaction (5)[l]

From these values it may be seen that most of the constants calculated from thermal data are many times larger than the experimentally determined ones. Although the experimental values may be somewhat low due to the disturbing influence of side reactions, they agree with one another with fair precision and it is generally considered that they represent more nearly the true conditions. The fact that the calculated values for K_p do not accurately indicate the actual experimental conversions at equilibrium does not entirely discredit their use as approximations in determining the advantage or futility of pursuing research on a reaction.

Catalysts

During the period which has just been covered by a review of the researches of Fischer, Tropsch and others, similar investigations looking to the synthesis of methanol had been in progress. The announcement was made by Calvert[132] in 1921 that the production of methanol from water-gas on a commercial scale with yields amounting to 80 per cent of theory

[131] a. Kelley, *Ind. Eng. Chem.* **18**, 78 (1926); 21 353 (1929); b. Smith, *ibid.* **19**, 801 (1927); c. Francis, *ibid.* **20**, 283 (1928); d. Ghosh and Chakravarty, *Quart. J. Indian Chem. Soc.* **2**, 142 (1925); e. Christiansen, *J. Chem. Soc.* **128**, 413 (1926); f. Lacy, Dunning and Storch, *J. Am. Chem. Soc.* **52**, 926 (1930); g. Smith and Branting, *ibid.* **51**, 129 (1929); h. Newitt, Byrne and Strong, *Proc. Roy. Soc.* **123A**, 236 (1929); i. Lewis and Frolich, *Ind. Eng. Chem.* **20**, 285 (1928); j. Audibert and Raineau, *ibid.* **20**, 1105 (1928); k. Brown and Galloway, *ibid.* **20**, 960 (1928); l. Smith and Hirst, *ibid.* **22**, 1037 (1930).

[132] Calvert, *Chem. Age (London)* **5**, 153 (1921).

had been accomplished but details in regard to the exact nature of the process were withheld. In Germany and France, particularly, developments were under way, the nature of which have been disclosed in patents issued in 1923 to Patart [138] in France and in 1925 to the Badische Anilin u. Soda Fabrik [134] in Germany.

The work done by the Badische Anilin u. Soda Fabrik covers a relatively long period of years, the first patents being issued in 1913 and 1914. These describe the preparation of hydrocarbons and their oxygen derivatives by passing mixtures of the oxides of carbon along with hydrogen or compounds containing hydrogen over suitable catalysts at high temperatures and at pressures of more than five atmospheres. The nature of the product which was obtained depended upon the type of catalyst and upon the other conditions of the experiment and varied greatly with variations in these factors. The catalysts which were first mentioned represented a large number of elements and their compounds, viz. cerium, chromium, cobalt, manganese, molybdenum, osmium, palladium, titanium, tungsten, and zinc. These elements were to be employed in different states of aggregation, such as powder, filings, wool, gauze, etc., or in the form of their oxides or other compounds. They could be present as mixtures in various combinations by weight. To these mixtures basic substances, such as the alkali hydroxides, carbonates, etc., could be added to advantage. Various carriers such as asbestos, pumice, and magnesium oxide were suggested. Poisons, such as sulfur in various states of combination, had to be avoided by purifying the reacting gases. Iron in any part of the surfaces of the apparatus exposed to the reacting gases was to be avoided. These warnings also occur repeatedly in all succeeding patents. Temperatures which are mentioned in the examples given, range from 250° to 420° C. and pressures from 50 to 120 atmospheres. The proportions of $CO : H_2$ by volume vary from $2 : 3$ to $2 : 1$.

It is obvious, at once, that the specifications mentioned in these patents are very broad in their scope and seem designed to cover the use, as catalysts, of practically all combinations of the elements and their compounds with the single exception of iron. In succeeding patents [185] specific combinations of different catalysts together with details regarding the methods employed in their preparation have been given for the synthesis of methanol relatively free from other products in distinction to the early patents which claimed mixtures. The notable changes that had been made in the process in order to obtain pure methanol are to be found chiefly in the nature of the catalysts used. Instead of the metallic oxide type of catalyst which was promoted by the addition small amounts of an alkali, catalysts of the same general type but without the alkali were proposed.

[138] Patart, *Chimie et. industrie* 13, 179-85 (1925); *Bull soc. encour. ind. nat.* 137, 141-73 (1925); *Compt. rend.* 179, 1330 (1924).
[134] I. G. Farbenindustrie, A. G., *Z. angew. Chem.* 40, 166 (1927); Elworthy, *Can. Chem. Met* 9, 139-40 (1925).
[185] Brit. Pats. 227,147 (1924); 228,959 (1925); 229,714 (1925); 229, 715 (1925); 231,285 (1925); 237,030 (1925); 238,319 (1925); 240,955 (1925), Badische Anilin u. Soda Fabrik.

In general mixtures of two or more metallic oxides with the more basic in preponderance and with copper as one of the metals were used.[136]

The investigations of Patart [133] in France have also been covered by specific patent [137] claims. The best yield of 2.5 gallons of methanol from 1000 cubic feet of water-gas compares advantageously with the 0.84 gallons of synthol obtained by Fischer from the same quantity of gas. Patart claims that no product of similar purity and yield (94 per cent of theory) could have been manufactured under any of the patents issued by the Badische Anilin u. Soda Fabrik prior to the dates of his patents. His first attempts to synthesize methanol in 1921 "were based upon van't Hoff and Le Chatelier's law for the displacement of the equilibrium point." It occurred to him that the reversible reaction:

$$CO + 2H_2 \;\; \underset{\longleftarrow}{\overset{\longrightarrow}{}} \;\; CH_3OH$$
$$\text{3 vols.} \qquad\qquad\qquad \text{1 vol.}$$
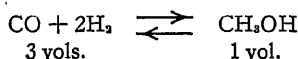
should proceed in the direction of the formation of methanol if the pressure on the system were increased. He considered further, that the secondary reactions leading to the formation of methane, water, and carbon dioxide (since they involved no change in volume) would not be favored by a rise in pressure and that, therefore, if the temperature were not too high the methanol could be removed from the system before it had a chance to go over to methane by the reactions [138]

$$CH_3OH + CO = CH_4 + CO_2$$
$$CH_3OH + H_2 = CH_4 + H_2O.$$
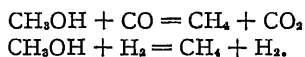
The best catalyst was found to consist of zinc oxide and copper (or copper oxide) with an admixture of compounds of chromium. The success of the operation depended upon (a) the absence of alkali, which would cause decomposition of the methanol and the production of higher alcohols and oily products, and (b) the complete elimination of all metals except copper, aluminum and tin from those parts of the apparatus which come in contact with the reacting gases. Contact of carbon monoxide with iron, nickel, or cobalt had to be avoided since they formed volatile carbonyls which deposited metal, by decomposition, on the active catalyst surface and thereby acted as poisons to destroy activity.

Catalysts composed of the following oxides have been found to be inert to the synthesis: alumina, silica, molybdenum oxide (Mo_2O_5), vanadium oxide (V_2O_3), blue tungsten oxide (W_2O_5), thoria, titania (TiO_2), magnesia, lime, barium oxide, and strontium oxide.[139] At a pressure of 150 atmospheres and a space velocity * of 5000 conversions of

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[136] a. Brit. Pat. 227,147 (1925); French Pat. 571,354 (1924) Badische Anilin u. Soda Fabrik. b. U.S. Pat. 1,558,559 (1925) Mittasch and Winkler. c. Frolich, Fenske, Taylor and Southwick, *Ind. Eng. Chem.* 20, 1327 (1928).

[137] French Pats. 540,343 (1922); 571,355 (1923) Patart.

[138] Lormand, *Ind. Eng. Chem.* 17, 430-32 (1925).

[139] Audibert and Raineau, *Ind. Eng. Chem.* 20, 1105-10 (1928).

* Space velocity $= \dfrac{\text{Vol. of gas (N.T.P.)}}{\text{(vol. of catalyst)(hour)}}$

less than 2 per cent were obtained with cerous oxide (Ce_2O_8), black uranium oxide (UO_2), beryllium oxide (BeO), and zirconium oxide (ZrO_2). Manganous oxide (MnO) and chromium sesquioxide (Cr_2O_8) were somewhat more active giving conversions of carbon monoxide to methanol up to 5 per cent. Zinc oxide was found to be still more active and at 350° C. a 17.5 per cent conversion was obtained. Such single component catalysts are very sensitive to temperature and overheating results in a rapid loss in activity. Multicomponent catalysts, on the other hand, not only give increased yields of methanol but also resist high temperatures or prolonged heating better.

In general, the best methanol catalysts have been found to consist of zinc oxide-copper oxide, zinc oxide-chromium oxide, or zinc oxide-copper oxide-chromium oxide in various ratios. Catalysts consisting essentially of copper are very poor for the synthesis.[188] Although the results of Audibert and Raineau show copper to be an active catalyst it is possible that inclusions of alkali from the preparation may have been a contributing factor. [139, 140] Copper oxide as a catalyst is also quite sensitive to sulfur poisoning.[141] As zinc oxide is added to the copper catalyst the activity markedly increases until a composition corresponding to between 60 and 70 mol per cent zinc is reached after which the activity again decreases to a lower value for pure zinc oxide. These same relations hold for zinc-chromium catalysts.[142] Thus, the best catalysts appear to be those containing a metallic oxide which is incompletely reduced under the conditions of the synthesis.

The technical and patent literature contains references to hundreds of different types of catalyst mixtures which are to be used under a wide variety of conditions. Although the earlier patents of Patart and the Badische Anilin u. Soda Fabrik specifically claimed the complete exclusion of iron from the system, a point which has aroused considerable controversy and litigation, it has been claimed that catalysts consisting essentially of iron may even be used for methanol synthesis.[148]

Studies of the decomposition of methanol over various catalysts show that the same catalysts are active toward the decomposition reaction at pressures of one atmosphere as are active toward the synthesis at the higher pressures.* Indeed, to Patart is attributed the statement that the results from the work of Sabatier on the catalytic decomposition of methanol led directly to the use of certain of the methanol synthesis catalysts.[188, 144] Smith and Hawk [145] found that zinc oxide made by igniting the carbonate, mixtures of zinc and chromium oxides in the atomic proportions of 4 zinc to 1 chromium, mixtures of zinc and uranium oxides,

[140] *Compare* Frolich, Fenske, Perry and Hurd, *J. Am. Chem. Soc.* **51**, 187 (1929).
[141] Audibert, *Ann. Comb. Liquides* No. 2, March-April 1930, p. 239.
[142] Cryder and Frolich, *Ind. Eng. Chem.* **21**, 867 (1929).
[148] a. Brit. Pat. 254,760 (1926) Badische Anilin u. Soda Fabrik. b. U.S. Pats. 1,608,643, 1,609 593. 1,625,924-5-6-7-8-9 (1926) Woodruff and Bloomfield.
* Chapter I.
[144] Frolich, Fenske, and Quiggle. *ibid.* **20**, 694 (1928).
[145] Smith and Hawk, *J. Phys. Chem.* **32**, 415-24 (1928).

mixtures of zinc and vanadium oxides, and mixtures of cadmium and chromium oxides were good catalysts for the decomposition of methanol into hydrogen and carbon monoxide at 300° C. and one atmosphere of pressure. Methanol was converted almost quantitatively to dimethyl ether in the presence of an alumina catalyst at temperatures up to 350° C. and atmospheric pressure.[146] At higher temperatures the formation of oxides of carbon, ethylene and methane increased rapidly. With a zinc oxide catalyst, however, only negligible amounts of dimethyl ether were formed. At temperatures above 325° C. the decomposition occurred with formation of gaseous products. At temperatures in the range of 270° to 430° C. it was possible to hydrate the ether and synthesize methanol in the presence of the alumina.[147] Catalysts which have mild dehydrogenating properties, such as copper, induce the formation of methyl formate from methanol at temperatures in the range of 150° to 250° C. and atmospheric pressure.[148]

Even at temperatures as high as 360° C. zinc-copper catalysts containing about 90 mol per cent copper oxide induce decomposition in such a way that 80 per cent of decomposed methanol appears in the product as methyl formate.[149] At this same temperature pure copper catalysts do not promote this reaction so strongly and about half of the methanol decomposed appears as methyl formate and half as formaldehyde. With copper oxide

$$CH_3OH = H_2CO + H_2$$
$$2H_2CO = HCOOCH_3$$
$$H_2CO = H_2 + CO$$
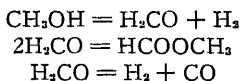
catalysts containing less than 10 mol per cent of zinc oxide and with as much as 30 per cent of methanol decomposed per pass less than 5 per cent of the methanol decomposed appeared as carbon monoxide in the products.

Catalysts such as metallic iron, nickel, cobalt, platinum and palladium, which promote the decomposition of methanol at low pressures also promote the reactions:

$$2CO = C + CO_2,$$
$$CO + 3H_2 = CH_4 + H_2O,$$
$$2CO + 2H_2 = CH_4 + CO_2,$$
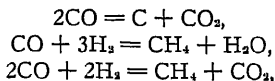
which all occur with a decrease in volume and which are, hence, forced to the right by pressure. For this reason such metallic catalysts, although active in causing the reduction of carbon monoxide, are worthless for the purpose of producing methanol. This is especially true since the equilibrium conditions favor these side reactions more than the methanol reaction.

[146] Adkins and Perkins, *J. Phys. Chem.* **32**, 221-4 (1928).
[147] *See also* U.S. Pat. 1,602,846 (1926) Burke.
[148] *See also* French Pat. 673,337 (1928) Compagnie de Bethune.
[149] Frolich, *J. Soc. Chem. Ind.* **47**, 173T (1928).

Mechanism

The simplest possible product that it is possible to form by the interaction of one molecule of hydrogen with one molecule of carbon monoxide is formaldehyde.

$$H_2 + CO = H_2CO \quad (2000 \text{ cal.*}).$$

The subsequent reduction of this formaldehyde by another molecule of hydrogen may lead to the formation of methanol, the next product which can form without rupture of the molecule.

$$H_2CO + H_2 = CH_3OH \quad (24,685 \text{ cal.}).$$

Continued reduction of the methanol by hydrogen leads to the splitting out of water and the formation of methane.

$$CH_3OH + H_2 = CH_4 + H_2O \quad (50,000 \text{ cal.}).$$
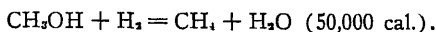
Interaction of methanol and carbon monoxide to form carbon dioxide and methane occurs with a still larger heat evolution.

$$CH_3OH + CO = CH_4 + CO_2 \quad (60,282 \text{ cal.}).$$
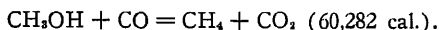
The fact that the two last reactions, representing a loss of methanol and reactant gases, occur without a change in the number of molecules and with a large evolution of heat made it difficult to stop the reaction at the methanol stage until specific catalysts had been developed. The effect of pressure in directing the reaction to the formation of methanol as indicated by the first two reactions is apparent when it is considered that either of the two reactions leading directly to the formation of the hydrocarbon, methane, occur with a decrease in the number of molecules of only two to one, whereas the methanol reaction occurs with a decrease of three to one. The effect of pressure in altering adsorption phenomena at the surface of the catalyst probably accounts for the relative ease with which the last two reactions are avoided.[150]

The presence of formaldehyde was recognized in the early work with the synthesis of oxygenated compounds from water-gas, and was probably accountable for because of insufficient activity of the catalysts to push the reaction to methanol exclusively at a rapid rate.[151] Indeed subsequent patent claims disclose that with high rates of flow, rapid cooling of product, and weak catalysts formaldehyde may be produced from hydrogen and carbon oxides.[152]

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* Heats of reaction are for all components in the gaseous state.
[150] Taylor and Kistiakowsky, *J. Am. Chem. Soc.* 49, 2468-76 (1927), give data on adsorption with zinc chromium catalysts.
[151] Brit. Pat. 20,488 (1913) Badische Anilin u. Soda Fabrik.
[152] a. Brit. Pat. 180,016 (1922) Lush. b. U.S. Pat. 1,460,244 (1923); Brit. Pat. 179,951 (1923) Heinemann. c. *Compare* U.S. Pat. 1,740,141 (1929) Arsem assr. to Commercial Solvents Corpn.

Chapter V

Oxidation of Methanol to Formaldehyde

A consideration of the synthesis and decomposition reactions of methanol shows that only low conversions to formaldehyde may be obtained by the direct catalytic decomposition of the alcohol. This is contrary to the case of ethanol and the higher alcohols, where good conversions to aldehydes or ketones may be obtained by direct dehydrogenation in the presence of directive catalysts. In the case of methanol, catalysts and temperature conditions conducive to the dehydrogenation of the alcohol to formaldehyde are also conducive to the decomposition of the aldehyde to hydrogen and carbon monoxide. Thus, Sabatier and Mailhe [1] mention that in the presence of copper a 50 per cent conversion of methanol to formaldehyde by direct dehydrogenation with only a 5 per cent loss is possible. However, this conversion was possible only with freshly reduced copper oxide. This catalyst rapidly lost activity and to obtain reaction it was necessary to use temperatures so high that large decomposition losses occurred. Thus, at 300° C. the decomposition of formaldehyde to hydrogen and carbon monoxide is quite marked and at 350° C. almost complete.[*][2]

$$CH_3OH = H_2CO + H_2 = CO + 2H_2.$$
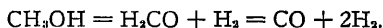
The decomposition is endothermic and to dehydrogenate the alcohol, heat must be supplied. However, if oxygen, usually in the form of air, is supplied to the reaction and the process conducted in the presence of certain metallic catalysts, such as finely divided copper or silver, high yields of formaldehyde may be obtained and the reaction made exothermic. It is by this oxidation process that practically all of the formaldehyde is produced. This process, although apparently simple, requires close temperature control and regulation of the extent of reaction to prevent undue losses of raw material.

Today formaldehyde finds widespread use in the hardening of gelatin, preservation of food, disinfection, tanning of leather and, most important, in the production of resins by condensation with phenol (bakelite) and in the synthetic organic chemical industry.

The investigations of Hofmann,[3] Tollens,[4] Loew,[5] Trillat, and Orloff

[1] Sabatier and Mailhe, *Ann. chim. phys.* 20, 344 (1910).
[*] *See also* Chapter III, page 68, *et seq.*
[2] *Compare* Tropsch and Roelen, *Chem. Zentr.* 1926, I, 3298.
[3] Hofmann, *Ann.* 145, 357 (1867); *Ber.* 11, 1686 (1878).
[4] Tollens, *Ber.* 15, 1629 (1882); 16, 917 (1883); 19, 2133 (1886).
[5] Loew, *J. prakt. chem.* (2) 33, 321-351 (1886).

on the oxidation of methanol have already been mentioned in connection with the historical survey of catalytic oxidation processes as applied to the alcohols in general. Some discussion of the special methods which were followed by these investigators may, however, be in order before proceeding to a discussion of the later developments in this field. The net results of the work done in the earlier period may be fairly represented by a description of the method used by Loew.[5] In this process a current of dry air was drawn as quickly as possible through a half-liter flask half filled with methanol and then through a hard glass tube 30 cm. long containing a cylinder of coarse copper gauze 5 cm. long. After leaving this tube the gases were passed successively through an empty flask of 300 to 400 cc. capacity and then through two similar flasks half filled with water. That part of the hard glass tube which contained the copper gauze was surrounded with brass gauze and gently heated. When the alcohol vapor reached the copper, the latter glowed more or less according to the rate at which the oxidizing mixture passed over it. The operation required no attention beyond keeping up the supply of alcohol and could be left day and night. A 15 to 20 per cent solution of formaldehyde was obtained in this way.

Trillat[6] noted that the action of the catalyst depends to some extent upon the power which it possesses to condense a given vapor or gas and that this power is at its maximum when the metal is present in its most finely divided condition. The intensity of the action of platinum, for example, was found to vary in the following order: sponge > colloidal > black > sheet or wire. The apparatus used by Trillat was similar to that described by Loew except that the catalyst was heated by means of an electric current passed through the spiral metal catalyst. The products formed as a result of the reaction were found to depend chiefly upon the temperature of the spiral.[7] Thus at 200° C. methanol was converted principally into methylal; at dark red heat (about 400° C.) methylal and formaldehyde were formed, the former varying from 0 to 50 parts in every 100 parts by weight of the latter; at cherry red heat (about 600° C.) these products were replaced by acids; and at a bright red heat (about 900° C.) more extensive decompositions with the formation of carbon dioxide occurred.

In the presence of porous bodies, such as pumice, unglazed porcelain, etc., impregnated with platinum black, the formation of methylal was not observed and the reaction product varied very considerably in the relative proportions of aldehyde and acid which were formed. The catalyst was prepared by treating pieces of pumice the size of a cherry, first with sodium hydroxide and then with sulfuric acid. After washing thoroughly and drying, these were impregnated with platinum black which was obtained by precipitation from solutions of platinum chloride. The product

[6] Trillat, *Bull. soc. chim.* (3) 27, 797 (1902).
[7] Trillat, *Bull. soc. chim.* (3) 29, 35 (1903); Ger. Pat. 55,176 (1890).

yield which was obtained in this way was, however, poor and the method was dangerous because of the possibility of explosions.

With a copper catalyst yields of 48.5 per cent formaldehyde were obtained by Trillat at 330° C. when the air stream carried 0.26 grams of methanol per liter. In the development of this process it was found that higher temperatures could be used to obtain higher rates of conversion. At present, temperatures of about 500° C. are used with copper catalysts.

In other experiments, a conical jet of alcohol vapor warmed under pressure was allowed to escape into the catalyst by means of a small orifice and was projected directly against the contact material, the air being admitted through a similar and separate opening. Brochet [8, 9] describes a form of apparatus which is similar to that of Trillat's and states that if the methanol contains water vapor the reaction takes place with explosive violence. The possibility of obtaining explosive mixtures and the necessity for getting correct proportions of air and alcohol were soon recognized.[10] Devices were perfected to permit adequate mixing of alcohol vapor and air (or oxygen-nitrogen mixtures) and consisted essentially of coke-filled towers maintained at a uniform temperature to which alcohol and air could be admitted at definite rates. The homogeneous mixture of methanol, oxygen, and nitrogen, preheated at 45° to 50° C., was then passed into the catalyst chamber.

Orloff's detailed investigations of the phenomena concerning the oxidation of methanol were preceded by a preliminary and very thorough examination [11] of the following catalysts: (1) Coke containing finely divided reduced copper on its surface and in its pores. This was made by soaking small pieces of coke in a solution of copper nitrate and then calcining and heating in the presence of a mixture of the vapors of hydrogen and methanol. The catalyst so prepared had a mottled red and yellowish-green appearance. It had practically no action on alcohol except in the presence of air, but by drawing a current of air through methanol kept at 60° C. and then passing the mixed gases over the catalyst contained in a chamber and heated at 380° to 420° C., it was found that about 39.78 per cent of the alcohol reacted to form formaldehyde and 15.9 per cent decomposed to yield oxides of carbon. (2) Asbestos coated with reduced copper. This was a very energetic catalyst but the yield of formaldehyde was very low because the decomposition of formaldehyde to hydrogen and carbon monoxide was also promoted. (3) Asbestos coated with a mixture of cerium sulfate and thoria. This catalyst had practically the same action as asbestos coated with reduced copper. (4) Platinized asbestos. This was such a powerful catalyst that the temperature had to be kept down to 95° to 98° C. and even so, the action resulted in the decomposition of the greater part of the aldehyde which formed, giving

[8] Brochet, *Compt. rend.* **119**, 122 (1894); **121**, 133 (1895).
[9] *Also compare* Kusnezoff, "Formaldehyd, seine Darstellung, seine Eigenschaften und seine Anwendung."
[10] Ger. Pat. 106,495 (1899) Klar and Schulze.
[11] Orloff, *J. Russ. Phys. Chem. Soc.* **39**, 1024 (1907).

yields at best of only about 10 per cent of the desired product. (5) Metallic platinum. Platinum wire heated in a glass tube at 330° to 400° C. acted well, yielding 41 per cent of formaldehyde. (6) Iron filings. A length of about 5 cm. of iron filings (10 grams) heated to a dark red glow in a copper tube gave a small yield of formaldehyde and a large deposit of carbon. Orloff stated further that in all of these cases the yield was improved by passing the mixture of methanol and air through a copper coil (undoubtedly acting catalytically) heated by one or two Bunsen burners, prior to its contact with the catalyst under investigation.

The results of this investigation confirmed quite largely the former findings of Sabatier and his fellow workers in regard to the dehydrogenating action of metal and metal oxide catalysts. At temperatures of about 350° C. such metals as iron, cobalt, nickel, platinum, copper and such oxides as those of aluminum, manganese, zirconium, zinc, titanium, silicon, glucinum, and cadmium had been found to exert a dehydrogenating action, to a greater or lesser degree, on methanol.

This decomposition reaction is endothermic, requiring the external addition of heat for the maintenance of temperature. The addition of oxygen to combine with the hydrogen liberated by the decomposition was hence rather a means of supplying heat than a means for forming formaldehyde chemically. An examination of the thermal changes involved in the oxidation of methanol to formaldehyde showed Orloff that the process as a whole was exothermic. Reasoning on the basis of this observation, he came to the conclusion that the reaction once initiated should be self-sustaining without the further application of external heat and proceeded to verify experimentally the truth of his deductions. In order to establish the requisite conditions a current of air was drawn through 89 to 90 per cent alcohol which was heated at 53.5° to 55° C. The mixed vapors of air and alcohol had a temperature of 42° to 43° C. and the vaporized alcohol had a purity of 99.5 to 100 per cent. In order to maintain this purity of the vaporized alcohol no more than about 25 per cent of the alcohol solution was allowed to distill in this way and when this proportion had distilled a fresh solution of the 89 to 90 per cent strength was substituted. The mixture of gases was passed over two or three rolls of freshly reduced copper gauze having a total length of 10 to 15 cm. and a total weight of 20 to 30 grams, contained in a glass tube 16 mm. wide by 830 to 850 mm. long. This contact tube was surrounded by a sheet iron jacket lined with asbestos. The operation was started by heating the tube to 300° C. but as soon as the mixture of alcohol and air began to pass through it, the heating was discontinued since the copper on contact with the entering gases immediately became red-hot and continued to maintain the temperature throughout the experiment. Under these conditions 48.45 to 49.25 per cent of the alcohol reacted to form formaldehyde. The gases formed as a result of the reaction consisted of carbon dioxide, a little carbon monoxide and about 20 per cent hydrogen. This exit gas

mixture burnt with a blue flame and was used to heat the tube in starting the operation.

In experimenting with a copper catalyst it was found that too long a layer of the catalyst promoted the decomposition of the aldehyde and that it was therefore better to increase the width rather than the length of the contact material. Thus an increase in the length of copper gauze from 10 to 15 cm. to 20 cm. was found to have an unfavorable effect on aldehyde yield.* It was also found that the strength of methanol in the distillate must not fall below 98 per cent because if this happened the catalyst became too hot and unfavorable decomposition occurred. The methanol must not contain more than 2 per cent of acetone as even this amount tended to decrease the yield. The copper must be freshly and completely reduced since otherwise it would not properly catalyze the reaction. The glass tube may be replaced by a copper tube but in this case external heating had to be resorted to periodically during the operation in order to maintain the catalyst at the most favorable temperature. Attempts to replace the copper by platinum or by iron filings gave unsatisfactory results and combination of copper gauze with platinum proved only slightly better. Asbestos impregnated with the lower oxides of vanadium was stated by Orloff [12] to be second in efficiency to freshly reduced copper. Dilution of the air with carbon dioxide was found to have an unfavorable effect upon the reaction while the yield of aldehyde was increased by dilution with methane and carbon monoxide.

An improvement in method was made by introducing into the forward end of the catalyst chamber "ignition pills" [13] prepared by soaking pieces of pumice first in H_2PtCl_6 dissolved in methanol, drying, calcining and then saturating with a solution of $PdCl_4.2NH_4Cl$, the operation of soaking and calcining being repeated several times. Instead of pumice stone, asbestos soaked with the platinum and palladium black and pressed into balls could be used. The mixture of methanol and air on reaching the kindling catalyst, ignited spontaneously and the copper gauze began to glow without the external application of heat. Another improvement consisted in first passing the formaldehyde through a tall column rectifier kept at 41° to 42° C., and then through another condenser to collect the unchanged methanol which was then recirculated.

The oxidation of methanol starts below 300° C. in the presence of a catalyst and quantities ranging up to 60 per cent of the total amount used in any experiment are decomposed. Not far from the oxidation temperature of the alcohol, formaldehyde undergoes decomposition into carbon monoxide and hydrogen. As much as 50 per cent of the formaldehyde which is formed may decompose in this way under certain conditions and in the presence of certain catalysts. The oxidation of hydrogen to water

* *Compare* Ref. 24.
[12] a. Orloff. *J. Puss. Phys. Chem. Soc.* 39, 855 (1907); 40, 796-9 (1908); *compare* b. U.S. Pats. 1,709,853 (1929); 1,735,763 (1930); Brit. Pats. 291,419 (1927), 296,071 (1927) Jaeger, assr. to Selden Co.
[13] Orloff, *ibid.* 40, 796 (1908).

and carbon monoxide to carbon dioxide occurs simultaneously with the decomposition of formaldehyde and the heat liberated thereby serves to increase the temperature of the contact substance, causing a further decomposition of the aldehyde.[14]

Theoretically, one pound of pure methanol requires 26.7 cu. ft. of dry air measured at 32° F. and 760 mm. of mercury pressure for oxidation to formaldehyde. This proportion can be attained only approximately in practice by bubbling air through methanol since even if the liquid methanol is maintained at the temperature to give the correct vapor pressure, complete equilibrium between air and methanol is not easily obtained without the use of long gas travel. It has been found, however, that considerable variation of this theoretical ratio does not seriously alter the conversion.

LeBlanc and Plaschke [15] found that the best temperature for operation with a silver gauze catalyst was 450° C. measured near the end of the mass. This is not the maximum catalyst temperature, however, since the forward end is usually at a red heat. At this temperature and with an increasing air to alcohol ratio, the yield of formaldehyde reaches a maximum and then decreases. The maximum yield was found to occur at a ratio of 0.46 grams oxygen per gram of methanol in the feed mixture. Above this oxygen ratio the loss of alcohol increases rapidly and constantly as the oxygen is increased. With a copper gauze 80-90 mm. long the best mixture was found to be 0.39 grams oxygen per gram of methanol. These oxygen ratios check closely with the value of 0.4 to 1 stated by Orloff [16] to be the best. These values are both lower than the amount of oxygen theoretically required (0.5 to 1) for the oxidation of the methanol.

LeBlanc and Plaschke [15] state that the amount of hydrogen in the gases from the reaction exceeded the sum of the carbon monoxide and carbon dioxide. This fact led them to propose the dehydrogenation mechanism. Orloff states that under favorable conditions of operation hydrogen represents 19 to 20 per cent of the gas volume, and that the proper course of the reaction could be followed by the amount of hydrogen formed.

It has been the practice to decrease the amount of oxygen or air used, even at the expense of conversion per pass in order to prevent side reaction losses. For good operation the inert gases should contain 3.5 to 4 per cent carbon dioxide, very little carbon monoxide, and no methane.[17] Such operation indicates very little loss by the decomposition of formaldehyde.

Theoretically 100 grams of pure methanol should yield 93.75 grams of pure formaldehyde, equivalent to 256.9 grams of 40 per cent formaldehyde solution. In practice about 82 per cent of theory is realized. High yields of over 90 per cent are possible only in laboratory apparatus or for short periods of time in commercial apparatus.[18]

[14] *Compare* Orloff, *J. Russ. Phys. Chem. Soc.* **40**, 1590 (1908); *Ber.* **42**, 895 (1909); *Chem. Zentr.* 1909, I, 984.
[15] LeBlanc and Plaschke, *Z. Elektrochem.* **17**, 45-57 (1911).
[16] Orloff, *J. Russ. Phys. Chem. Soc.* **39**, 1414-39 (1907).
[17] Siegel, *Chem. Ztg.* **51**, 782 (1927).
[18] Ullmann's "Enzyklopädie der Technischen Chemie," 2nd Ed., vol. 5, p. 417.

The oxygen in the formaldehyde process probably plays a multiple rôle by (1) furnishing heat through reaction with hydrogen and thus maintaining the temperature level necessary for the endothermic dehydration reaction, (2) lowering the partial pressure of the hydrogen and thus permitting greater decomposition through the reversible dehydrogenation reaction, and (3) increasing the activity of the catalysts by inducing a process of alternate oxidation and reduction. Practically all of the early workers recognized the fact that the essential reaction was one of dehydrogenation and that the use of oxygen was as an auxiliary to facilitate the process. The original theory considered the process as essentially one of direct oxidation. Secondary oxidation to formic acid, carbon dioxide, and water was postulated, but as no formic acid was identified and as free hydrogen usually appeared in the product this theory was short lived. The success attending the application of the dehydrogenation theory to the formaldehyde process has led to the attempted adaptation of it to other oxidation processes some of which it has not been so well suited to, however.[19]

The experiments of Ghosh [20] have disclosed interesting features of the dehydrogenation process. A copper catalyst prepared by precipitating the hydroxide from the acetate by sodium hydroxide, drying at 110° C., and reducing with hydrogen at 180° C. began to decrease in activity after 17 hours of use and after 22 hours had only a half of its original activity. With a space velocity of 900, and temperature of 195° C. the efficiency was 64.6 per cent at the end of 17 hours. A catalyst prepared from copper sulfate had only a quarter of the activity of the acetate catalyst. The addition of less than one per cent of nickel as a promoter increased the initial activity but decreased the life. Addition of silver lowered the activity. Small additions of thorium resulted in increased activity and prolonged life but as the amounts added were increased decomposition of formaldehyde to hydrogen and carbon monoxide occurred. With a catalyst containing 0.1 per cent cerium nitrate an efficiency of 73.4 per cent (corrected for 9.4 per cent unchanged methanol) was obtained after 36 hours of operation with a space velocity of 1774, and a furnace temperature of 200° C.

Iron-iron oxide catalysts have been repeatedly reported to be unsatisfactory for methanol decomposition or oxidation, because of their activity in causing complete oxidation to carbon dioxide or decomposition to carbon if a deficiency of oxygen prevails. However, catalysts composed of iron and molybdenum oxide have been found to be very efficient for methanol oxidation.[21] Such a mixed catalyst apparently combines the excellent directive power of molybdenum and the activity of iron. Molybdenum oxide deposited on small iron balls was shown to be 100 per cent efficient

[19] *Compare* Jobling, *Chem. World* III, 1914. No. 8, 232, 255, etc.
[20] a. Ghosh and Chakravarty, *Quart. J. Indian Chem. Soc.* 2, 142-9 (1925) (equilibrium). b. Ghosh and Baksi, *ibid.* 3, 415-30 (1926), (catalyst); *British Chem. Abstract* (A) Feb. 1930, p. 172 (poisons).
[21] Adkins and Peterson, *J. Am. Chem. Soc.* 53, 1512-20 (1931).

toward the oxidation of methanol to formaldehyde. Although no side reactions occurred with this catalyst, only about 38 per cent conversions of entering methanol could be obtained after a steady state of catalyst activity had been obtained. The amount of methanol converted was a linear function of the amount of methanol passed over the catalyst per unit of time. Not more than 10 per cent of the available oxygen could be consumed no matter how large the excess of alcohol or how long the time of contact. From a mechanism standpoint this apparently indicates that for this particular catalyst, adsorption of methanol at the active surface is as essential as adsorption of oxygen.

With air-methanol mixtures of 93 liters of air per 10 grams of alcohol the catalyst composed of equal atomic amounts of iron and molybdenum permitted an initial conversion of 82 per cent. The activity, however, increased over a period of 23½ hours and the conversion rose to 90.8 per cent. This value is comparable with that obtained by Thomas [24] with copper, silver, and gold catalysts. However, considerably higher yields could be obtained with the iron-molybdenum oxide catalyst at these high conversions. The reactor which was used in the experiments had a cross section of 50 × 6 mm. (I.D.) and a 15 cm. depth of catalyst was normally used. The experimental procedure was a departure from that previously used in methanol oxidation experiments. Whereas most of the other experimental work had been done under autothermal conditions with the commonly used gauze catalyst attaining whatever temperature it might under the conditions of feed rate and air ratio, these recent tests were conducted with a U shaped, flat aluminum catalyst tube immersed in an electrically heated sodium-potassium nitrate bath, with temperature under accurate control. With this apparatus and an air-methanol ratio at 93 liters per 9 grams, conversions of 85.2, 91.8, and 91.9 per cent were obtained at 353°, 373°, and 400° C. respectively. At these conditions efficiencies were 90.0, 90.7 and 85.3 per cent. More carbon monoxide than dioxide appeared in the gaseous reaction products.

Where oxygen is introduced with the methanol vapors over a copper catalyst, it has been observed that the freshly reduced copper assumes a rose color showing that oxidation occurs in the presence of methanol vapor at 400° C. Results appear to be about the same whether the gaseous mixture of alcohol and air is preheated or not. The walls of the tube used in preheating should be of fire-brack, glass or porcelain if the elimination of catalytic action upon the contained gases is desired.[22] In cases where the gases are not preheated the length of the contact mass may be lengthened and the temperature raised from 300° to 400° C. When preheating is employed, the diameter of the contact may sometimes be increased with favorable results. The catalyst acts by becoming alternately oxidized by oxygen and reduced by the hydrogen liberated in the decompo-

[22] *Compare* Ipatiew's "Pyrogenetische Kontaktresktionen," *J. Russ. Phys. Chem. Soc.* **35**, 577, 599, 603, 606 (1903) and earlier.

sition of the alcohol. Besides the main reaction, the decomposition of formaldehyde occurs as a side reaction. It is this side reaction which represents the main source of loss of alcohol and it must be kept at a minimum. The hydrogen and carbon monoxide liberated in this way also become oxidized and the heat generated in this way may cause excessive temperatures to be reached in the catalyst bed.

Although the oxidation-reduction mechanism apparently holds for such oxidation catalysts as oxides of copper, nickel, cobalt, manganese, molybdenum, vanadium, etc., it cannot be offered as the simple mechanism for the case of such metal oxide catalysts as are not readily reduced to the metal or lower oxide. To obtain pertinent data for such catalysts Lowdermilk and Day [28] studied the oxidation of methyl and ethyl alcohols, ethylene, benzene, and toluene in the presence of the oxide of samarium. The results indicated that the presence of the rare earth oxide with copper promoted oxidation. However, the net effect was to give no advantage over a copper catalyst since the oxidation tends to go too far. The best yields of formaldehyde were obtained with an alcohol-oxygen ratio of 1 gram to 0.3-0.31 liter. The actual yields obtained with copper-pumice catalysts never dropped below 85 per cent compared with 72 per cent obtained by Thomas.[24] The reason for the higher yield is attributed to the fact that 15 mm. length only of catalyst was used whereas Thomas used a 74 mm. length which gave more opportunity for decomposition.

When pure samarium oxide was used as the catalyst the process yields were very low. This fact combined with the fact that the catalyst temperature was always very high, above 600° C. even with very low air rates, indicates that the catalyst was very active. The analytical results indicated that at the high catalyst temperature the initially formed formaldehyde rapidly decomposed to hydrogen and carbon monoxide. When an excess of oxygen was used the further oxidation of formaldehyde also occurred.

A fairly large number of other processes which describe the conversion of methanol into formaldehyde are to be found in the literature. The use of silver deposited on copper wire or gauze and of a silver spiral alone has already been referred to in the preceding chapter.[17, 25] In this work Plaschke obtained yields of 58 per cent with silver and of 55.4 per cent with copper at temperatures of 455° C. and with a space velocity of almost 4000. Various adaptations of this form of catalyst have been described and patented. For example, Bobrov [26] found that when vapors of methanol and air were passed over copper gauze spirals, yields of formaldehyde which varied between 37 and 42 per cent were obtained, while if these were

[28] Lowdermilk and Day, *J. Am. Chem. Soc.* **52**, 3535-45 (1930).
[24] Thomas, *J. Am. Chem. Soc.* **42**, 867 (1920).
[25] a. Plaschke, Doctor's Dissertation, University of Leipzig (1909) may be secured through H. Gravel and Co., 33 King St., Covent Garden, London, W. C. b. Piccard, *Helv. Chim. Acta* **5**, 147 (1922). c. Wöhler, Herzog's "Chem. Tech. der organ. Verbindungen," Heidelberg (1912), p. 557; (1927), p. 764. d. Ger. Pat. 286,731 (1913) Verein für chemische Industrie; *J. Soc. Chem. Ind.* **35**, 73 (1916).
[26] Bobrov, *J. Russ. Phys. Chem. Soc.* **50**, 130 (1918); *J. Soc. Chem. Ind.* **42**, (A) 329 (1923).

replaced by copper gauze discs which were packed perpendicularly to the axis of the tube, the yields increased to 67.6 to 71.6 per cent. The yields obtained with coppered, silvered and gilded asbestos used in conjunction with copper discs were respectively 70 to 72, 77.7, and 72.8 per cent. Acetone up to 4 per cent was said not to interfere with the reaction. Pure methanol used with a silver catalyst gave a yield of 89.5 per cent formaldehyde but the product polymerized almost immediately. Somewhat different results were obtained by Thomas.[24]

The results of Thomas give a basis for comparison of the relative efficiency of catalysts of copper, silver and gold. The experiments were performed with pure methanol and the air-methanol vapor mixture was preheated to 100° C. prior to admission to the catalyst which was preheated to 400° C. but not heated during the runs. The work was on the basis of a constant air rate, that is, a constant rate of supply of oxygen to the catalyst. The catalyst temperature varied with the ratio of oxygen to alcohol in the feed. It was found that the temperature varied from 350° to 565° C. but that the catalyst was hottest near the entrance. Measurements with a thermocouple in a special gold gauze catalyst disclosed that actual temperatures vary from 530° to 900° C. in the hottest section of the catalyst. The results of the work replotted on a single graph are shown by Figure 7.

With catalysts of metal gauze rolls as described under Figure 7, air to alcohol ratio equivalent to 0.25 grams oxygen per gram of alcohol, and air rates of about 125 liters per hour the copper, silver and gold catalysts in the order named gave the following conversions and yields, respectively, 88.5 and 40 per cent, 95 and 55.5 per cent, and 90.4 and 49.7 per cent. With the copper catalyst best yields were obtained at 0.55 to 0.65 grams oxygen per gram of alcohol but at this high air ratio the yields were low. The silver catalyst was characterized by the fact that large variations in gas speed had little effect on the reaction at constant mixture compositions in spite of apparently large temperature differences at the catalyst. With this catalyst the decomposition to carbon oxides was low and the yields were correspondingly high. The gold catalyst had a much greater tendency to decompose methanol than did silver. The total loss to decomposition increased directly as the rate of air feed. As the length of the gold gauze roll was increased the decomposition of formaldehyde increased slightly, and it was evident that the oxidation reaction was complete in the first 20 mm. of length.

A comparison of these three metal catalysts shows that on the basis of total methanol reacted the silver catalyst was more active than the copper which was more active than the gold. Since the silver catalyst was also least active toward the decomposition of formaldehyde to hydrogen and carbon monoxide, it was recommended as the most desirable.

Patents based on the use of silver (or silver along with copper, or rhodium or platinum or any metal of the platinum group) have been taken
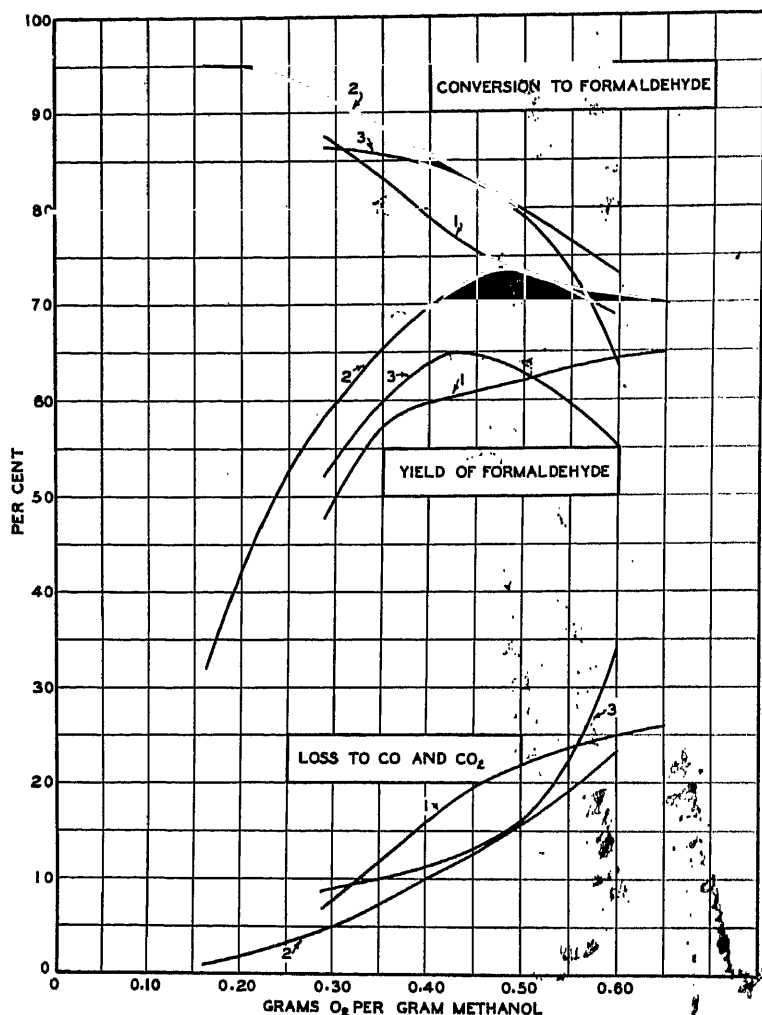
FIG. 7.—Oxidation of methanol to formaldehyde by air.[24]
Curve 1. Copper catalyst—74 mm. long, 14 mm. diameter, 30.5 grams, 61 mesh gauze. Air rate of 115 to 140 liters per hour.
Curve 2. Silver catalyst—102 mm. long, 13 mm. diameter, 40.75 grams, 61 mesh gauze. Air rates varying over the wide range of 90 to 230 liters per hour.
Curve 3. Gold plated copper catalyst—100 mm. long, 14 mm. diameter, 31.35 grams copper, 2.40 grams gold, 35 mesh gauze. Air rate at 150 liters per hour.

out by Hochstetter.[27] Hochstetter attempted to define catalysts that had a combination dehydrogenation and oxidation action. The yields which were claimed varied from 70 per cent for pure copper to 96 per cent for

[27] Fr. Pat. 467,076 (1914); Brit. Pat. 464 (1914); Swedish Pat. 41,459 (1916); U.S. Pats. 1,100,076 and 1,110,289 (1914) Hochstetter.

silver coated with very small amounts of platinum. The combination of metals used in the catalysts were not in the form of alloys but in the form of a base metal with the auxiliary metal deposited on it. Another process patented by Blank [28] claims silver precipitated on asbestos as a catalyst and states that the amount of undecomposed alcohol which passes over with the reaction gases is so small as to be almost negligible. In still other patents [29] a similar method of oxidation is applied to the construction of a formaldehyde lamp. In this case flax thread is immersed in silver nitrate solution from which the silver is then precipitated by the addition of formic acid. The flax after drying is carefully combed and placed in the chimney of a carefully constructed methanol lamp. The mechanism is arranged in such a way that after a preliminary lighting hot vapors of methanol and air pass continuously through the chimney and maintain the silver at a red heat.

A silver (or copper) catalyst suitable for the oxidation of methanol may also be prepared by heating silver or copper cyanide or a mixture of these in the presence of air to the point where puffing occurs. By incorporating a ferro- or ferri-cyanide, e.g., bismuth ferro-cyanide, bismuth ferri-cyanide, calcium cerium ferro-cyanide, cerium cobalt ferro-cyanide, vanadium or molybdenum ferro-cyanide with the starting material, an activated product may be obtained. The silver or copper cyanides are prepared by precipitating a soluble cyanide with silver nitrate or cupric chloride respectively. [30]

The use of different metals which are capable of acting as oxidation catalysts was further explored by Fokin. [31] Such catalysts may be prepared by impregnating a porous inert carrier such as coke, pumice stone or alundum, with a solution of copper, nickel, iron formate, etc., drying and heating in an atmosphere of hydrogen to reduce the formate at the lowest possible temperature. [32] Platinized asbestos for use as a catalyst may be prepared by dissolving platinum in aqua regia, evaporating the solution to dryness, extracting the residue with hydrochloric acid, neutralizing the solution with sodium carbonate, mixing it with a paste of asbestos and distilled water and finally reducing at 60° C. with formic acid. The product is then washed, dried, carded and separated into flakes. [33] Fokin found that the conversion of methanol to formaldehyde ranged from a low value of one per cent for a nickel catalyst, up to 84 per cent for a copper-silver alloy, with the other catalysts arranged as follows in increasing order of activity; aluminum, manganese, cobalt, platinum, copper, silver, and gold. The yield of formaldehyde in terms of percentage of methanol reacted is not explained, but probably refer to percentages of the theoretical yield by weight.

[28] Ger. Pat. 228,697 (1908); Fr. Pat. 418,349 (1909) Blank.
[29] U.S. Pat. 1,067,665 (1913) Kusnezow; Fr. Pat. 412,501 (1910) Bouliard.
[30] Brit. Pat. 163,046 (1920) Clancy, assr. to the Nitrogen Corpn.
[31] Fokin, *J. Russ. Phys. Chem. Soc.* 45, 268 (1913); *Chem. Zentr.* 1913, I, 2016.
[32] U.S. Pat. 1,122,811 (1914) Snelling.
[33] Brit. Pat. 120,551 (1918) Frabetti.

In the production of formaldehyde by most of the methods which have been described up to this point, relatively pure materials and temperatures up to 400° C. or higher are required. If, however, vanadium pentoxide is used as the catalyst the claim has been made [34] that it is possible to produce better yields of formaldehyde, that the catalyst is not affected by poisons such as acetone and water, that the reaction takes place at a sufficiently low temperature to be below the decomposition point of formaldehyde, and that, moreover, a large excess of air is beneficial to the reaction, thus minimizing the danger from explosions which take place only at certain concentrations of the alcohol-air mixtures. A temperature as low as 225° C. has been claimed to be used and methanol which contains as much as 5 per cent acetone is said to give satisfactory results.[35]

Claims have been made that by the maintenance of a substantially neutral reaction mixture throughout the formaldehyde process, the formation of by-products is greatly decreased. For this purpose a basic material such as ammonia is added to the reaction mixture prior to the conversion.[36] Rapid cooling is used to prevent the formation of paraformaldehyde.

The principal catalyst poisons have been found to be oils, organic chlorine, or sulfur-containing compounds which usually enter with the air used for the oxidation.[17, 20b] The presence of acetone in the methanol had been found to be objectionable but with the substitution of the very pure synthetic alcohol for the product of wood distillation this difficulty has disappeared. Water vapor in appreciable quantities serves to decrease the temperature of the catalyst and hence, to slow down the reaction. Some patents have even claimed the addition of steam for the purpose of controlling the reaction rate.

Several patents have been issued which refer to the preparation of formaldehyde by the oxidation of such substances as ethanol, glycerol and acetaldehyde. It has been claimed that ethanol may be oxidized to formaldehyde by passing the vapors mixed with air over platinum at white heat.[37] Formaldehyde may also be formed by passing a mixture of vaporized glycerol or glycol and air over a copper wire gauze heated at 300° to 500° C. After the initial reaction, the process may become autothermal and yields of 30-35 per cent of aldehyde obtained. The copper gauze may be replaced by silver, iron, lead, antimony, manganese or the oxides.[38] In operations where acetaldehyde is used, the aldehyde is mixed with oxygen, air or gases containing oxygen and then passed over heated catalysts similar to those used for methanol oxidation or composed of the oxides of metals such as vanadium or cerium which are capable of forming a number of different oxides. According to the example which is described in the patent, the mixture of aldehyde and air passes over a coil of copper

[34] U.S. Pat. 1,383,059 (1921); Brit. Pat. 163,980 (1921) Bailey and Craver, assrs. to the Barrett Co.
[35] *See* Christiansen, *J. Am. Chem. Soc.* 43, 1670 (1921) for data on the effect of water vapor.
[36] U.S. Pat. 1,738,745 (1929); Brit. Pats. 336,282-3 (1930) Bakelite Corpn.
[37] Swiss Pat. 74,843 (1917) Perronne, *Chem. Abstracts* 12, 484 (1918).
[38] Jap. Pat. 39,153 (1921) Makajima and Kaisha.

wire netting heated at 450° C. at the rate of 0.5 liter per minute per sq. cm. of cross section.   The oxidation is of the type of flameless combustion and may be carried out in the presence of steam or other indifferent gases or vapors.   The product may equal 50 per cent of the decomposed aldehyde.[39]

From the data of Kharasch[40] the theoretical heat of reaction for the oxidation of methanol to formaldehyde is given by the equation:

$$CH_3OH(1) + 1/2 O_2(g) = H_2CO(1) + H_2O(1) + 36,800 \text{ cal.}$$
(32.04 grams)   (30.02 grams)
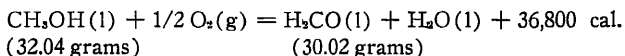
A portion of this heat serves to preheat the entering air-methanol vapor mixture to reaction temperature, a portion is lost by radiation from the catalyst chamber, and a portion carried out as sensible heat in the reaction products.   The decomposition of formaldehyde to hydrogen and carbon monoxide is endothermic and would use a portion of the heat particularly where this decomposition occurred to a large extent.   However, a portion at least of such liberated decomposition products are also oxidized and furnish more heat to raise the catalyst temperature or be dissipated.

During oxidation the entire contact mass is not raised to a red heat but only the forward portion upon which the incoming gases first impinge. This acts as catalyst for the primary reaction.   The secondary reactions are catalyzed by the rear, non-glowing portion of the contact which nevertheless cannot be eliminated because of its effect (by reason of its mass) in equalizing and controlling the heat distributed to the forward portion. In order for the catalyst to glow during the reaction its mass must be very compact so as to accumulate heat rapidly.   In order to function at the same time as an oxygen carrier, it must have a texture such as to offer the greatest possible number of impact areas to the incoming gas current.   With an insufficient catalyst mass, fluctuations in the feed rate may cause erratic operation due to constant fluctuation in temperature of the light catalyst mass with rate of feed.

Orloff found that increase in the mass of the catalyst beyond certain limits tended to lower its temperature as well as that of the gases impinging on it and in this way to slow down the reaction.   In any given operation he found that other factors being equal, that catalyst should be selected which for the least mass presents the greatest number of impact areas to the impinging gases, which at the same time affords a sufficient number of open spaces between the surfaces of the contact to permit the complete mixing of the reacting gases, and which in addition, possesses a heat capacity that approximates the average value found for the metals.   Copper fulfills these conditions well, and is used in preference to silver because of its lower cost.   While it is impossible to overestimate the importance of extensive impact areas combined with intervening spaces that provides for

[39] Brit. Pat. 178,842 (1923) Consort. Elektrochem. Ind. Ges.
[40] Kharasch, *Bur. Standards J. Research* 2, 359 (1929).

a thorough mixing of the gases, the maintenance of the catalyst at a temperature which favors the desired reaction is, of course, of even greater importance.

Several forms of apparatus have been patented for use in the oxidation of methanol. For example, the reaction chamber may be heated electrically by means of resistance coils which are carried on a frame which passes through and around it.[41] The air carburetted with methanol may be supplied to the reaction chamber by a process in which the alcohol is allowed to drop on the blades of a rotary fan which is connected with a heated air supply. The product passes from the reaction chamber to a
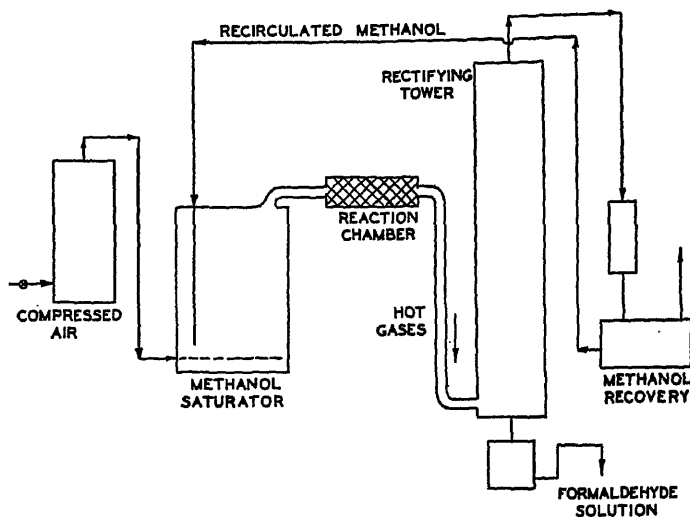
Fig. 8.—Apparatus for methanol oxidation.

cooler and thence to a saturator which is provided with rotary vanes that secure the continuous circulation of the absorbent liquid.[42] The carburetted air may have steam added for the purpose of regulating the temperature of the catalyst. The apparatus is specially characterized by the direct arrangement in series of the different units without intermediate piping. With this construction there is only a small volume of carburetted gas present at any time and should an accidental back-fire occur, there is no undue rise in pressure since the open inlet of the fan allows the free expansion of the gases. The operation of the plant is very readily controlled by regulating the feed of the alcohol, the air supply and the rate of circulation of the absorbing liquid.

The general type of apparatus used for the production of formaldehyde is shown in Figure 8. Compressed air is fed from a storage tank through

[41] Brit. Pat. 110,787 (1916) Bcake, Roberts and Co.
[42] Brit. Pat. 814 (1915); Fr. Pat. 480,597 (1915); Canadian Pat. 178,572 (1917); U.S. Pat. 1,213,740 (1917) Calvert.

a series of small holes into a layer of methanol maintained at the desired temperature for correct air-alcohol ratio. The vapor-air mixture passes directly to a reaction chamber which may, for example, contain six copper tubes 600 mm. long and 50 mm. in diameter in which are deposited rolls of copper wire gauze 110 mm. long. No heat is supplied externally to the catalyst except at the start of the process and the air rate and air-alcohol ratio are so adjusted that a temperature of 550° to 600° C. is maintained autothermally.[43] The hot gases and vapors are passed directly to a rectifying column from which the formaldehyde solution is withdrawn at the bottom, and the fixed gases containing methanol vapors at the top. The hot reaction mixture must be rapidly cooled after leaving the reaction chamber to prevent polymerization of the aldehyde and other secondary reactions. This is done by bringing it directly into contact with the relatively cool aqueous solution in the tower.[44] The methanol contained in the fixed gases is recovered and returned to the system.

Methanol containing very little formaldehyde may be obtained by the distillation of aqueous solutions which contain mixtures of the two substances in amounts up to 38 to 40 per cent. This distillate may then be used for subsequent oxidations. The residue from such a distillation contains only a trace of methanol.[45]

[43] *See also* a. *Chem. Rundschau Mittelcuropa u. Balkan* **1925**. 269; b. Vanino and Seitter, "Der Formaldehyde," 2nd Ed. (1927), Leipzig, Menzel, **1927**, 2nd Ed.
[44] U.S. Pat. 1,744,295 (1930) Ahlbeck, assr. to Bakelite Corpn.
[45] *Compare* Wilkinson and Gibson, *J. Am. Chem. Soc.* **43**, 695 (1921).

Chapter VI

The Oxidation of Gaseous Paraffin Hydrocarbons

AVAILABILITY OF RAW MATERIAL

Utilization of the enormous quantities of gaseous paraffin hydrocarbons by means of oxidation has been the object of much research. These hydrocarbons are available in tremendous quantities in natural gas, in the products from the cracking of petroleum, in coke oven gas, and in carburetted water-gas. The volume of methane, ethane, propane and butane available in the United States alone during the year 1927 has been estimated to have been over 2,472,000,000,000 cubic feet.[1] Table VII shows in

TABLE VII.—*Commercial Fuel Gases and Their Content of Gaseous Hydrocarbons.*[2]

Gas Source	Cubic Feet	Methane	Ethane	Propane	Butane	Ethylene	Propylene	Remarks About Composition
				Per Cent				
Natural gas	1,800,000,000,000 [a]	80	10	3	1			Estimated
Coke oven gas........	639,644,000,000 [b]	30	10	1		4		Estimated
Gas from petroleum distillation	270,000,000,000 [a]	61	21	12	4			[d]
Gas from cracking process	250,000,000,000 [a]	50	16	7	3	7	7	Estimated
Coal and water gas	210,743,000,000 [c]	13	3	0.3				[d]
Carburetted water gas..	112,186,000,000 [c]	14	3			12		Estimated
Oil gas	24,289,000,000 [c]	40	15			3		Estimated
Coal gas	7,411,000,000 [c]	31	2.0			6.5		Estimated
Propane and butane in natural gasoline	15,992,750,000 [d]			12.1	87.9			[d]
Propane and butane in refinery gasoline	15,865,550,000 [d]			20.8	79.2			[d]

Volumes of Gaseous Hydrocarbons from Commercial Fuel Gases.

Gas	Cubic Feet
Methane	1,976,718,840,000
Ethane	354,184,040,000
Propane	116,171,919,000
Butane	62,915,000,000
Ethylene	57,758,465,000
Propylene	17,500,000,000

[1] Egloff and Schaad, *Chem. Rev.* 6, 94 (1929).
[2] a. Egloff, *Ind. Eng. Chem.* 22, 790 (1930); b. "Mineral Resources of the United States 1925," part II, page 601; Separate II: 30, "Coke and By-Products in 1925"; c. "Dept. Commerce, Statistical Abstract of the United States 1926," p. 730 (data for 1925); d. Egloff and Shaad, *Chem. Rev.* 6, No. 1 (1929).

some detail the quantities of these gases available from different sources and also gives an estimate of the amounts of ethylene and propylene directly available.

Oberfell is quoted [3] as authority for the statement that there are available 13,000,000 gallons of propane and butane per day or about 4,750,-000,000 gallons per year from the natural gas industry. The cracking units of the petroleum industry in this country are potential sources of 900,000,000 gallons of propane and an equal volume of butane.[4] While discussing the sources and quantities of saturated hydrocarbons, it might be well to point out that the cracking industry produces large quantities of olefins.[5] The cracked gases formed by the vapor phase processes may contain as high as 55 per cent of unsaturated hydrocarbons, and although this figure is considerably higher than the average, the fact that about a third of all the gasoline used today is formed in cracking operations gives some idea of the potentialities of this source. Vapor phase cracking for the purpose of forming non-knocking gasolines, and the cracking of straight run gasolines and kerosenes for the purpose of improving their knock rating are being increasingly practiced with the result that the quantities of olefins being produced are increasing. The gases resulting from cracking operations have an average composition such as shown in Table VIII.

TABLE VIII.—*Composition of the Gases Formed in the Cracking of Petroleum.*

Gas	Liquid Phase	Vapor Phase
	Per Cent	
H_2	2.0–3.0	6.0–7.0
C_2H_4	3.0–4.0	25–30
C_3H_6	6.0–7.0	14–18
C_4H_8	5.0–6.0	6–10
Paraffins	80.0 ±	40 ±
Butadiene	Trace	Trace — 1.0

Although the present major use of these hydrocarbons is as fuel, the tremendous possibilities offered for conversion to valuable chemicals makes it interesting to consider the research work which has been done and some of the results that have been attained. By oxidation these gases may be converted to methyl, ethyl, propyl, and butyl alcohols; formaldehyde, acetaldehyde, propionaldehyde, and butryaldehyde; formic, acetic, propionic, and butyric acids; resins; etc. An idea of the potentialities of hydrocarbon oxidation may be obtained by considering the theoretical yields of alcohols

Alcohols	Approximate Gallons
Methyl	22,000,000,000
Ethyl	5,800,000,000
Propyl	2,600,000,000
Butyl	1,800,000,000

[3] *Natl. Petroleum News* **22**, No. 22, 27 (1930).
[4] *Chem. Met. Eng.* **37**, 354 (1930).
[5] *Compare* Dunstan, *J. Soc. Chem. Ind.* **49**, 320T (1930).

obtainable from the gaseous paraffin hydrocarbons readily available.[1] Many of the investigations, particularly the earlier ones, were carried out by simply heating mixtures of air or oxygen and the hydrocarbons. More recently attention has been directed to controlling the reactions to produce useful products and experiments with catalysts, chemical reagents, ozone, silent electric discharges, alpha radiation, etc., have been made, but apparently no commercially available process has been developed which can compete with present day methods for the preparation of the pure compounds. An exception to this is a commercial process yielding a mixture of methanol and aldehydes but regarding which practically nothing has been published (see page 177).

Mechanism   OXIDATION OF METHANE

The oxidation of hydrocarbon gases, especially methane, at atmospheric pressure has received considerable attention. The majority of this work has been devoted to consideration from the viewpoint of combustion phenomena, however, rather than for the purpose of forming valuable organic compounds, and hence, has been largely non-catalytic in nature. Nevertheless, much of this early work has been valuable not only as a source of valuable information but also as a stimulant to further research. The oxidation reactions are complex and a variety of products, chiefly water, carbon, carbon oxides and hydrogen usually result. At present a number of theories regarding the mechanism of the oxidation prevail, the best known of which is probably that of the stepwise formation of hydroxyl compounds, although the peroxide theory is rapidly gaining ground, particularly in connection with the study of fuels.

The early theory of methane oxidation assumed that carbon and water were the initial products of reaction or that hydrogen burned preferentially to carbon. However, in 1861 Kersten[6] declared that carbon monoxide and hydrogen were the primary products, and that although some free carbon may form at times, the carbon is normally oxidized to carbon monoxide before the hydrogen is reacted upon. This idea, later revived by Misterli,[7] involves the preferential combustion of carbon and is thus directly opposed to the hydroxylation theory. This theory might possibly apply to the case of acetylene combustion, since this hydrocarbon is sufficiently unstable as to explode alone under certain conditions, but cannot hold for the more saturated hydrocarbons which do not explode alone.

Armstrong[8] had suggested that oxygen combines directly with the methane molecule to form hydroxyl compounds, and that the oxygen acted as molecular oxygen resulting in the formation of dihydroxy hydrocarbon derivatives. He also postulated that water took part in the

[6] Kersten, *J. prakt. Chem.* 84, 311-317 (1861).
[7] Misterli, *J. Gasbeleucht* 48, 802 (1905).
[8] Armstrong, *J. Chem. Soc.* 83, 1088 (1903).

mechanism and formed hydrogen peroxide but could not adequately support his theory with facts.

In trying to confirm their theory in regard to the intermediate formation of oxygenated products during combustion, Bone [9] and his co-workers carried out extensive researches and from their work has come the present hydroxylation theory. According to Bone the oxidation of methane takes place in steps, methanol, formaldehyde, formic acid, and carbonic acid being formed in the order named. These various steps are indicated below. The double arrows point out the main course of reaction, while the single arrows show how the intermediate compounds may decompose.

$$
\begin{array}{lll}
 & CH_4 & \\
\underline{\text{decomposition}\quad} \quad \downarrow\downarrow & & \text{oxidation} \\
 & CH_3OH & \\
\downarrow & \quad \downarrow\downarrow & \text{oxidation} \\
CH_2O + H_2 & (CH_2(OH)_2) & \\
\downarrow \quad \text{decomposition} & \quad \downarrow\downarrow & \text{decomposition} \\
\underline{\downarrow\quad \text{decomposition}\quad} & CH_2O + H_2O & \\
CO + H_2 & \quad \downarrow\downarrow & \text{oxidation} \\
\downarrow \quad \text{decomposition} & HCOOH & \\
CO + H_2O & \quad \downarrow\downarrow & \text{oxidation} \\
\big| \quad \text{oxidation} & CO(OH)_2 & \\
\underline{\qquad\qquad\qquad} & \quad \downarrow\downarrow & \text{decomposition} \\
 & \rightarrow CO_2 + H_2O &
\end{array}
$$
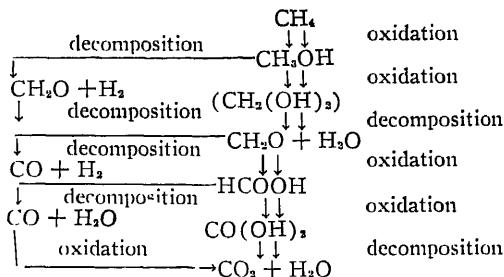
The theory thus supposes the successive conversion of hydrogen atoms to hydroxyl groups, followed by partial decomposition, to give in order alcohols, aldehydes or ketones, acids, carbon monoxide, carbon dioxide and water. All of the research work of these investigators, although quite voluminous, is interpreted in the light of this theory.

The formation of water and carbon in rapid hydrocarbon combustion, as in explosions, represents the best experimental evidence in support of this mechanism.[10] The failure of Bone to detect methanol among the oxidation products in his experiments weakens this theory considerably, however. The only intermediate compound that could be identified was an aldehyde which together with water usually appeared as the early product. This is true of the higher paraffins as well as of methane.

Alcohols have been detected among the products of hydrocarbon oxidation, however; but the processes in these instances were of such a type, either catalytic or under the influence of electric discharges, that the mechanism is somewhat beclouded. The amount of alcohol found has usually been quite small relative to the aldehyde and its presence is not distinct proof of its formation as a primary product.

Blair and Wheeler [11] by employing very rapid rates of gas flow were able to obtain considerable formaldehyde, but no methanol. They conclude that a short time of heating and a slow oxidation are the principal

[9] Bone, *Trans. Chem. Soc.* **61**, 871; **71**, 26, 46; **79**, 1042; **81**, 535; **85**, 693, 1637; **87**, 910, 1232; **89**, 652, 660, 939, 1614; **93**, 1198; *J. Chem. Soc.* **83**, 1074.
[10] Bone and Drugman, *J. Chem. Soc.* **89**, 660-71 (1906).
[11] Blair and Wheeler, *J. Soc. Chem. Ind.* **42**, 181-92T (1923).

factors in obtaining good yields of formaldehyde. Too vigorous an oxidation forms the aldehyde under conditions which promote its rapid decomposition, and excessive times of contact give too much opportunity for complete decomposition even when at a lower rate. For example, concentrations of two per cent of formaldehyde by volume do not decompose appreciably at 500° C. while concentrations above 0.2 per cent are completely decomposed at 720° C. It is to be noted in connection with this work that temperatures of 700° C. and higher were necessary for reaction.

In opposition to Bone's theory is that of Stevens [12] according to which any alcohol present is formed as a by-product rather than as an intermediate oxidation product. The latter theory is supported by a number of recent investigations demonstrating that alcohols are not formed, or at least have not been identified in the oxidation, at atmospheric pressure, of hydrocarbons ranging from methane to heptane.[13] Stevens believed that since the presence of water retarded the oxidation of hydrocarbons the mechanism of oxidation must involve the splitting out of water as a product. He consequently proposed that the hydrocarbon and oxygen combined to give an unstable molecule which subsequently broke down to water and an unsaturated oxygenated hydrocarbon. This unsaturated residue was then supposed to rearrange to an aldehyde or ketone.

The mechanism which has been postulated by Bone involves as the first step the formation of methanol from methane and necessitates the splitting of the oxygen molecule into oxygen atoms or ions, the separation of one of the hydrogen atoms from the carbon atom, and the introduction of the oxygen atom between the hydrogen and the carbon. It seems unlikely that the oxygen atoms even if formed from molecular oxygen under the conditions of the reaction would be sufficiently isolated to react individually with separate hydrocarbon molecules. It is more probable that the oxygen will react as a molecule with the methane to form water and formaldehyde directly.

The mechanism of this latter reaction has been interpreted by Bone, Davies, Gray, Henstock, and Dawson [14] according to the mechanism of Bone and Drugman as follows:

$$CH_4 + O_2 = [H_2C(OH)_2] = HCHO + H_2O = H_2 + CO + H_2O.$$
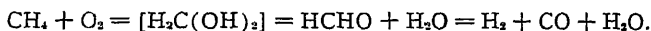
They exploded mixtures of methane and oxygen under pressures of ten to fifty atmospheres, and showed that the reaction velocity of methane with oxygen was at least twenty to thirty times as great as that of hydrogen. The same overall equation for the oxidation has been supported by Burgess and Wheeler,[15] who hold that there is a preferential

[12] Stevens, *J. Am. Chem. Soc.* **50**, 2523 (1928).
[13] a. Layng and Youker, *Ind. Eng. Chem.* **20**, 1049 (1928); b. Edgar and Pope, Swampscott meeting *Am. Chem. Soc.* (1928).
[14] Bone, Davies, Gray, Henstock, and Dawson, *Phil. Trans.* **215A**, 288-308 (1915).
[15] Burgess and Wheeler, *J. Chem. Soc.* **105**, 2598-2601 (1914).

burning of hydrogen rather than of carbon monoxide in all mixtures in which the ratio of oxygen to methane is greater than 1.5.

The hydroxylation theory has been criticized also by Callendar[16] on the basis of the necessity for splitting of the oxygen molecule, a step not likely to occur readily at the temperatures at which the slow oxidations are conducted. The lack of experimental evidence to support any mechanism involving the ionization of oxygen prior to or at the time of oxidation of a hydrocarbon is an additional factor in opposition to the idea that an alcohol is the primary oxidation product. At explosion temperatures, however, atomic oxygen may be present and effective as such. Actually most of the experimental work on the direct oxidation of methane with elemental oxygen has shown that water and formaldehyde are among the first reaction products, whereas methanol is not, and several processes[17] claim this reaction to form formaldehyde industrially.

That methanol has not been detected among the products resulting from the oxidation of methane in many of the experiments where its presence could logically be expected[18] does not necessarily preclude the fact that methanol may be the first product formed. Although methanol is stable to hydrogen and carbon monoxide at room temperature, its stability rapidly decreases with increase in temperature. At the temperature used in the oxidation experiments and at atmospheric pressure it is probable that methanol is practically completely dissociated into hydrogen and carbon monoxide.

Fig. 9.—Decomposition of methanol to hydrogen and carbon monoxide at atmospheric pressure.
Curve 1—after Kelley, *Ind. Eng. Chem.* 21, 353 (1929).
Curve 2—after Smith and Hirst, *ibid.* 22, 1037 (1930).

Reference to Figure 9 which is based on the best equilibria data available for the reaction

$$2H_2 + CO = CH_3OH$$

shows why this is so. In this connection it is interesting to note the quite different results obtained by oxidizing under high pressures (*cf.* page 175), conditions which presumably enable the stabilization of the methanol to be realized.

The fact that other investigators * working in the same temperature range but under somewhat different conditions have been able to detect methanol in the products from the reaction, seems to throw some doubt

[16] Callendar, *Engineering* 123, 147 (1927).
[17] a. Bone and Drugman, *J. Chem. Soc.* 89, 676 (1906); b. Wheeler and Blair, *J. Soc. Chem. Ind.* 42, 260-6T (1923); c. Gruszkiewicz, Austr. Pat. 7,279 (Aug. 23, 1913); d. Berl and Fischer, *Z. angew. Chem.* 36, 297-302 (1923); e. Lüttgen, Ger. Pat. a 40,701 and a 40,786; f. Kunheim, Ger. Pat. 205,774 (1907); g. Behrens, Ger. Pat. B73,089 (1913); h. Walter, Ger. Pat. 168,291 (1904); *Allgem. österr. Chem.-Tech. Ztg.* 29, 23; *Chem. Zentr.* 1911, 1440-1.
[18] Frolich, Harrington, and Waitt, *J. Am. Chem. Soc.* 50, 3216 (1928).
* *See* section on "Oxidation in Presence of Nitrogen Oxides," p. 184.

on this explanation for the absence of methanol in some of the reported experiments. Although such discrepancies might be explained on the basis of differences in methods of temperature measurement, in times of contact, in rates of cooling, in analytical procedure, etc., it is more difficult to account for the relatively large yields of formaldehyde obtained, if the methanol supposedly first formed, decomposed rather than oxidized. It will be necessary for the relative rates of the different steps to be determined before any definite conclusions may be drawn.[19]

Even if methanol were first formed from the interaction of atomic oxygen and methane and did not decompose, it would have a tendency to be oxidized preferentially to methane due to the fact that the three remaining hydrogen atoms would be labilized by the presence of oxygen in the molecule and would hence be much more susceptible to reaction than the unlabilized hydrogen atoms of methane. This fact is partly brought out by the heats of reaction involved in the formation of the products in the different steps, shown in Table IX.

TABLE IX.—*Heats of Combustion of Methane and Intermediate Products.*

Gas Phase Reaction	Heat Evolved [20] gm. cal./gm. mol	Heat Evolved per mol O_2
$CH_4 + 1/2\,O_2 = CH_3OH$	31000	62000
$CH_3OH + 1/2\,O_2 = CH_2O + H_2O$	35235	70470
$CH_2O + 1/2\,O_2 = HCOOH$	65780	131560
$HCOOH + 1/2\,O_2 = CO_2 + H_2O$	57845	115690

Thus the reactions involving the addition of successive atoms of oxygen to the molecule become more and more exothermic for each addition. This effect alone makes it difficult to stop the oxidation reaction at any point short of complete combustion.

Methane is very unreactive and the introduction of the first oxygen atom would require a high temperature level on this account. The introduction of successive oxygen atoms requires successively lower temperature levels. The net effect is that at the temperature required for the initiation of any particular oxidation step the oxidation of the next lower oxidation product can go forward with a greater tendency. This results in a phenomena similar to the fall of a stone in a vacuum in that the farther it goes the higher the rate of fall becomes.

Opponents of this view point to the fact that methanol has been detected, and that some workers [13a] have found the higher alcohols more difficult to oxidize than the corresponding hydrocarbons. In the case of methane oxidation, methanol has been detected in experiments in which homogeneous mixtures of oxidizing gas and hydrocarbon containing insufficient oxygen for complete combustion had been used. The fact that practically no oxygen remained in the effluent gases in these experiments

[19] *Compare* Fort and Hinshelwood, *Proc. Roy. Soc.* 129A, 284-99 (1930).
[20] a. "Heats of Combustion of Organic Compounds," Kharasch, *Bur. Standards J. Research* 2, Feb. 1929; Research Paper, No. 41; b. Latent heat of vaporization, "*International Critical Tables,*" 5, 135, 138.

accounts for the inability of the methanol reported present to ·oxidize further. Regardless of the tendency for a reaction to occur the rate at which it goes on will determine the ultimate result. It is perfectly possible for reactions to have a considerable tendency to react and yet have immeasurably slow rates. As an example one might indicate the reaction of hydrogen and carbon monoxide to form methanol, which has a great tendency to occur at room temperature and yet which does not occur to any appreciable extent under such conditions. It is well admitted that methane occupies a unique position in the paraffin hydrocarbon series because of its unreactive nature and it is difficult to see that because methyl, ethyl, butyl, and amyl alcohols are much less readily oxidized by air than hexane and similar hydrocarbons [16] that they would stand in the same relation to methane. Indeed, Bone and Stockings have shown that ethanol is even more readily oxidized than ethane.[21]

On the other hand this view is well supported by the experimental evidence of the processes themselves. In all of the work only low conversions to formaldehyde have been obtained. Thus Tropsch and Roelen [22] studied the effect of composition of the gas mixture, diameter of reaction tube, temperature, and time of contact. Their best results were obtained with 4.0 mm. reaction tubes, a time of contact of about 1/1000 second, a temperature of 1000° C., and a methane concentration of 16 per cent. Under these conditions the yield was 1.2 per cent of the theoretical. At lower temperatures the conversion of methane to formaldehyde was higher but the formaldehyde in the reaction mixture extremely low, and as the temperature was raised, although the conversion of methane to formaldehyde decreased, the absolute quantity of formaldehyde produced became greater.

The steps in the oxidation subsequent to the formation of aldehyde conform to Bones' theory in that the aldehyde oxidizes further to formic acid, decomposes into carbon monoxide and water, or oxidizes to carbonic acid which decomposes to carbon dioxide and water.

When it is considered that oxidation reactions may be conducted in the presence of various solid and gaseous catalysts, under the influence of electrical discharges, under alpha radiation, etc., it will be realized that no one theory can be expected to account for the diverse results. Indeed it is reasonable to suppose that the mechanism may be quite different in the different cases. However, in all the methods so far proposed, if any oxygenated compounds at all are formed, aldehydes are present. This would indicate that the aldehyde stage is intermediate in all of the processes.

In the oxidation of methanol to formaldehyde the gaseous reaction products always contained the oxides of carbon, along with nitrogen, methane, varying quantities of free hydrogen and a small but persistent

[21] Bone and Stockings, *Proc. Chem. Soc.* 20, 106 (1904).
[22] Tropsch and Roelen, *Brennstoff Chem.* 5, 37-42 (1924).

quantity of free oxygen. The formation of these products attracted the interest of even the earliest investigators of catalytic oxidation phenomena and the fact was almost immediately established that the same catalysts which have the power to accelerate oxidation processes are also able to catalyze the decomposition of formaldehyde to hydrogen and carbon monoxide. For example, when finely divided copper is used in the oxidation of methanol, good yields of aldehydes may be obtained at temperatures up to 280° C. Above this temperature the rate of decomposition of the aldehyde increases rapidly and at 360° C. the substance dissociates completely into these two components.[23] It may be said in general, that all finely divided metals behave in this way but that for any given temperature the action of the metal is selective. For example, at temperatures below 250° C. the use of copper is practical because it accelerates the dehydrogenation of methanol,

$$CH_3OH = H_2CO + H_2$$
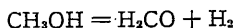
without affecting the rate of decomposition of the product in any very marked degree. Finely divided nickel, on the other hand, is impractical because while it is a much better dehydrogenation catalyst than copper, it also accelerates the decomposition of the aldehyde so that the actual yield of the desired product is very low. Recent investigations of the equilibrium relationships in the system:

$$H_2CO = CO + H_2,$$
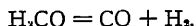
between 150° and 350° C. show that the relative amount of decomposition depends markedly upon the nature of the catalyst. In the case of a copper catalyst the concentrations of the individual components of the system at different temperatures as determined by experiment are in agreement with the theoretical as determined by calculations based on Nernst's formula.[24]

In general it may be said that alcohols undergo dehydrogenation when heated (with or without the presence of free oxygen) to give the corresponding aldehyde and along with it varying quantities of hydrogen, carbon monoxide, carbon dioxide, and saturated hydrocarbons. The oxygen present in the ordinary oxidation process may serve only as a means of regenerating the catalyst, especially if it is of the type easily oxidized and reduced such as copper. With such a catalyst for the oxidation, continuous formation of copper oxide takes place with subsequent reduction to metallic copper by combustion of the alcohol, formaldehyde, carbon monoxide, or hydrogen. Waiving the fact that in the case of the higher members of the alcohol series, other types of decomposition are also possible, as, for example, dehydrations to unsaturated compounds and to ethers—it seems desirable to restate some of the conclusions which were arrived at by

[23] Sabatier, *Compt. rend.* 148, 1734-36 (1909).
[24] Ghosh and Chakravarty, *J. Indian Chem. Soc.* 2, 142-9 (1925).

Ipatiew as a result of his study of the phenomena of dehydrogenation of ethanol and which have already been referred to in some detail in an earlier chapter.*

Ipatiew, perhaps more than any of the earlier investigators in the field of catalytic oxidations, appears to have been conscious of the fact that variations in the nature and physical state of the catalyst, in the temperature, pressure, and time of contact were directly responsible not only for the equilibrium relationships represented by the main reaction, but for equilibria between the different individual products which were formed as the result of decompositions and subsequent interactions. He pointed out, for example, that when alcohol is heated under pressure in an iron tube, the percentage of hydrogen present in the reaction mixture steadily increases with increase in temperature up to a certain limit and then falls off regularly. At the same time the percentages of carbon monoxide and carbon dioxide first increase and then decrease irregularly. The percentage of gaseous saturated hydrocarbons increases steadily and fairly rapidly with increase in temperature. This was accounted for by Ipatiew as due (a) to an increase in aldehyde decomposition, and at relatively low temperatures corresponds to a decrease in the total amount of liquid products, and (b) to the tendency of both oxides of carbon to undergo reduction to methane in the presence of hydrogen and finely divided metals which act as accelerators for this reaction. Thus a certain definite portion of the increase in the percentage of saturated hydrocarbons among the reaction gases was observed to correspond to a decrease in the percentage of carbon monoxide and hydrogen.

Because of the extremely complicated nature of hydrocarbon partial oxidation and the consequent various equilibrium relationships that may exist between the different components of the systems, it becomes necessary to study each of these possible relationships individually in order that a complete picture of the whole may be obtained. This has been done to some extent in the other chapters of this book.

Wieland [25] was very successful in applying the dehydrogenation theory to the oxidation of alcohols and should possibly find application of the theory in the field of hydrocarbon oxidation. Similarly the dissociation theory of Nef [26] for organic chemical reactions might quite reasonably be involved. Formic acid is present in the methane flame and may be detected by rapidly cooling certain portions of the flame to stop further reactions and condense the formic acid. Wieland [25] has presented the hypothesis that this formic acid is formed by the decomposition of the methane to carbon and hydrogen and the immediate reaction of the carbon with water to give carbon monoxide by the water gas reaction. This carbon monoxide then reacted to give the formic acid. Methane will also react directly with water to give mixtures of hydrogen and carbon oxides.

* Chapter II.
[25] Wieland, *Ber.* 45, 2606-15 (1912).
[26] a. Nef, *Ann.* 298, 202 (1897); b. Jones, *Proc. Am. Chem. Soc.* 39, 44 (1917)

This phase of the problem of natural gas utilization will be discussed more completely in a later section.

In formulating a theory for the production of formic acid from methane in the presence of metallic oxides such as copper suboxide at temperatures ranging from 200° to 500° C., Nielson [27] assumed the intermediate formation of carbon monoxide and water which then reacted to formic acid as follows:

$$2CH_4 + 3O_2 \nearrow \begin{array}{c} CO_2 + 2H_2O \\ \searrow \\ CO + H_2O + H_2 \\ \searrow \swarrow \\ HCOOH \end{array}$$
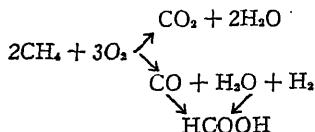
Recently the formation of peroxides has received considerable attention particularly in regard to knocking in internal combustion engine cylinders [28] and in the drying of unsaturated vegetable oils. Since the advent of the high speed, high compression automobile engine and the introduction of anti-detonating fuels for use in them, considerable research has been carried out on a study of the mechanism involved in the combustion of the hydrocarbons used as the fuels. As a result of this work considerable evidence has been accumulating which indicates a chain type of reaction for these oxidations. Since this work, as well as that dealing with peroxide formation, has largely dealt with higher hydrocarbons of the order usually found in gasoline and has had as its object the attainment of ends other than the formation of oxygenated hydrocarbon compounds, a discussion of this phase of the general problem is reserved for another part of this book.

Catalytic Oxidation of Methane

A great number of catalysts have been tried in the oxidation of methane at atmospheric pressure with the hope of obtaining intermediate products of oxidation. It appears, however, that catalysts tend to carry the reaction to equilibrium, at which state methanol, formaldehyde and formic acid are present in only extremely minute traces. This is well illustrated by the work of Wheeler and Blair,[11] who studied the influence of catalysts in connection with their work on the mechanism of combustion. When methane was oxidized in the presence of metallic and metallic oxide catalysts, no formaldehyde could be detected even at very short times of contact. The formaldehyde produced in the circulation experiments was in a concentration much greater than that required for equilibrium in the reaction:

$$HCHO = H_2 + CO.$$
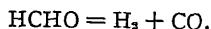
Rapid cooling made it possible for some to be isolated before equilibrium could be attained or further oxidation occur. With catalysts, however,

[27] Nielson, *Beama* 12, 34-35 (1923); Brit. Pat. 198-385 (1923) Nielson and Laing.
[28] a. Callendar, *Engineering* 123, 147, 182, 210 (1927); b. Moureu, Dufraisse and Chaux, *Chimie et Industrie* 18, 3 (1927); c. Mardles, *J. Chem. Soc.* 1928, 872; *Compare* Chapter XI.

the true equilibrium may be attained almost instantly at the temperature necessary to oxidize methane. The reaction products, however, gave no indication that catalysts changed the course of the oxidation of methane, and indicated that short times of contact were essential to recovery of formaldehyde. Surfaces had a similar but less pronounced action than the catalysts, and formaldehyde could be detected when they were used.
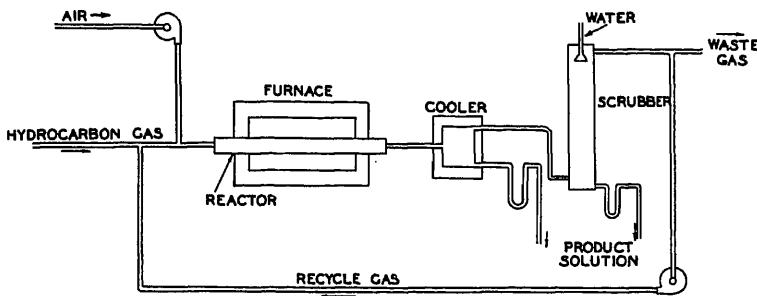
FIG. 10.—General arrangement of apparatus as used in the oxidation of hydrocarbon gases to aldehydes, etc.

Catalysts are most frequently used for their influence in increasing the rate of a given reaction. They have no influence on the final state of equilibrium of a system but hasten the attainment of that state during reaction. Where several reactions of different type may occur side by side, catalysts of a selective nature are used to direct the reaction over the desired path. This direction of the course of a reaction is the result of a speeding up of the desired step to the exclusion of the other steps which might also occur. In considering the catalysis of oxidation reactions particularly of aliphatic hydrocarbons at atmospheric pressure it must be recognized that the oxidation reactions are probably stepwise with each successive step occurring with greater ease. The type of reaction for the different steps is the same, so that a catalyst which will accelerate the first step will also accelerate the successive steps. It is difficult to conceive of a catalyst that will accelerate the rate of oxidation of methane to formaldehyde and not at the same time accelerate the oxidation of formaldehyde to formic acid or to water and carbon dioxide. It would seem therefore that the selection of a proper catalyst to enable the production of formaldehyde and other oxygenated products of methane with large yields as well as large conversions was an exceedingly difficult task. Nevertheless the literature is replete with the accounts of such attempts.

In carrying out experiments on the phenomena of flames in 1817, Sir Humphry Davy [20] discovered that a heated platinum wire inserted in a jar containing a mixture of gas and air above the explosive limit became red hot and continued so until the oxygen was practically consumed. This

[20] Sir Humphry Davy, *Phil. Trans.* 107, 77 (1817).

experiment and subsequent work served to show: (1) that gaseous combustion is speeded up at relatively low temperatures by hot solids, particularly when composed of the platinum group of elements and (2) that hydrogen is more readily burned than the other combustible gases. Perhaps the most profitable studies on the catalytic oxidation of low molecular weight paraffinic hydrocarbons have been those on the selective oxidation of particular constituents of mixtures for analytical purposes.

Probably the earliest experiments on the selective oxidation of combustible gas mixtures were carried out by Henry in 1825.[30] In a series of remarkable experiments Henry found that by properly controlling the conditions of combustion over a platinum catalyst, hydrogen and carbon monoxide could be entirely burned with only very slight oxidation of any hydrocarbon, such as ethylene or methane, which was present in the original mixture. He further showed that when a mixture of equal volumes of hydrogen, carbon monoxide, and oxygen was exposed to a platinum catalyst at an elevated temperature, 80 per cent of the oxygen united with the carbon monoxide and 20 per cent with the hydrogen and explained his results on the basis of the carbon monoxide poisoning the catalyst for the reaction between the oxygen and hydrogen.

Because of its former importance in the separation of hydrogen and methane in gas analysis, oxidation by palladium has been investigated repeatedly. Coquillon[31] early found that methane and air readily yielded oxidation products in the presence of red hot spirals of platinum or palladium. Hempel[32] reported that methane and oxygen did not burn in the presence of palladium at 100° C. but that reaction began at 200° C. When a mixture of hydrogen, methane, and air was passed over palladium at ordinary temperatures or at 100° C., the hydrogen alone burned and the methane remained unchanged provided the palladium was not allowed to heat up.[33] At temperatures as low as 200° C. the methane begins to be attacked. Winkler[34] stated that methane was not burned when passed over palladium asbestos in a tube at incipient redness, whereas Brunck[35] reported that in this method the thread of catalyst might glow without causing burning of the methane. These observations were possibly in error due to poor analytical procedure for the detection of oxidized products, since Nesmjelow[36] has found that palladium asbestos oxidized methane at as low a temperature as 150° C. Subsequent workers have placed the temperature for reaction at much higher temperatures. Thus, Phillips[37] found 405° to 451° C. to be the lowest temperature, and Denham[38] gave the temperature of 514° to 546° C. as that of incipient oxida-

[30] Henry, *Phil. Mag.* 65, 269 (1825).
[31] Coquillon, *Compt. rend.* 77, 445-6 (1873).
[32] Hempel, *Ber.* 12, 1006-8 (1879).
[33] Hempel, *Z. angew. Chem.* 25, 1841 (1912).
[34] Winkler, "Handbook of Technical Gas Analysis," Freiberg, Engelhardt, 1892, Vol. I, 145.
[35] Brunck, *Z. angew. chem.* 16, 695-7 (1903).
[36] Nesmjelow, *Z. anal. Chem.* 48, 254-5 (1909).
[37] Phillips, *Am. Chem. J.* 16, 164-73, 255-77 (1894); *Z. anorg. Chem.* 6, 213-59 (1894); *Trans. Am. Phil. Soc.* 17, (N.S.), 149 (1893).
[38] Denham, *J. Soc. Chem. Ind.* 24, 1205 (1905).

tion. Richardt [39] by very careful work found that over palladium wire at 450° C. little noticeable oxidation of methane occurred, but that at 700° C. there was rapid combustion. These wide differences in the reported results are undoubtedly due to differences in condition of the catalysts, differences in measuring and reporting temperatures, and possibly errors in analytical procedure.

Hydrogen is burned completely and methane is unaffected when mixtures of the two are passed over copper oxide at 250° C.[40] After use in analytical procedures the reduced material may be reoxidized by use of a current of air or oxygen. Since there is no necessity for dilution of the gases under examination with air or oxygen as is the case when palladium asbestos is used for this purpose, copper oxide is distinctly superior because of the added accuracy obtainable in subsequent determinations with the same sample.[41] While this reaction is not distinctly catalytic in that the solid phase is altered chemically during the process, it is entirely probable that the use of oxygen in the combustible gas mixture would permit the regeneration of the copper oxide during the reaction rather than subsequent thereto as recommended for the analytical procedure, and that the process could thus be made truly catalytic in nature.

The mechanism of this selective oxidation process has been interpreted by Bancroft [42] in the light of an adsorption surface. In reviewing the work of Henry, which is quoted at great length, Bancroft concludes that hydrogen must be more powerfully adsorbed by the platinum catalyst than methane or ethylene. Similarly, from the results of Lunge and Harbeck,[48] who found carbon monoxide to be attacked preferentially even to hydrogen, it was concluded that this gas was adsorbed to the greatest extent. The fact that Bone [9] has showed methane to be much more reactive than hydrogen when oxidized in borosilicate bulbs either by slow combustion at 300° to 400° C. or by explosion with an electric spark lends strong support to the selective nature of the catalysts employed in both cases, especially at the lower temperatures.

The catalytic oxidation of methane to form oxygenated products was suggested by Glock in 1898 and patented the following year.[44] Glock observed that Coquillon [81] had obtained formic acid by using hot platinum or palladium but had been unable to prove the presence of methanol or formaldehyde. He found that by using a more mildly acting contact substance such as granular copper, pumice, or asbestos that the lower oxidation products of methane could be obtained. A temperature of 600° C. was proposed and a cyclical process with condensation of products and reoxidation of unreacted methane contemplated. An arrangement of the reaction tubes in series allowed the reaction to proceed in stages. In the

[39] Richardt. *Z. anorg. Chem.* 38. 76-91 (1904); *J. Gasbeleucht.* 47, 566,590 (1904).
[40] Jaeger, *J. Gasbeleucht* 41. 764 (1898).
[41] *Compare* Dennis. "Gas Analysis" 1913. p. 199.
[43] Bancroft. *J. Phys. Chem.* 21. 644 (1917).
[48] Lunge and Harbeck. *Z. anorg. Chem.* 16, 50 (1898)
[44] Ger. Pat. 109,014-5 (1899) Glock.

first tube the heat of combustion of the methane was sufficient to maintain the catalyst in a glowing condition but the application of external heat was necessary in order to insure a reaction temperature of 600° C. in the succeeding tubes, since the gases before entering these chambers were very much diluted as a result of washing and of further additions of air. The advantages of this arrangement were said to consist in a slow rather than a rapid oxidation of methane and the maintenance of a moderate temperature during the reaction. The same results were obtained in oxidizing illuminating gas if the gases were first led through a tube containing a platinum catalyst maintained at 177° C. Under these conditions the hydrogen was oxidized while the methane remained unchanged.

Phillips [87] has carried out a very large number of experiments on the phenomena of the oxidation of hydrocarbon gases by air in the presence of finely divided metals and other oxidizing materials. The finely divided metal coated on asbestos, was placed in a glass tube of ⅛ inch bore, and the mixture of air and gas passed through the tube while the latter was gradually heated. It was shown that: (1) The temperature of oxidation is mainly dependent on the solid substances with which the gas is in contact. (2) Two phases are often, but not always, to be observed in the process of oxidation. As the temperature rises, a point is reached at which a minute and scarcely recognizable trace of CO_2 appears; and after this slow oxidation has continued for some time and gradually increased during a rise in temperature of 20° or 30° C., or even more, a sudden and intense reaction occurs. Very often the first slow oxidation is not observed. (3) The oxidation of a hydrocarbon by air under conditions similar in all respects, does not always occur at the same temperature, the variation in initial oxidation temperature being sometimes considerable (in some of the experiments exceeding 50° C.). A variation in the proportion of inflammable gas and air does not seem materially to influence the oxidation temperature. (4) The paraffins are the most stable towards air in presence of palladium, carbon monoxide and acetylene stand next in order, and the olefins are the most easily oxidized. (5) Of the members of the same homologous series, the lower are the more stable towards oxidizing influences. (6) Hydrogen stands alone among combustible gases in undergoing oxidation under the influence of palladium-coated asbestos in the cold. (7) Oxidation of gaseous hydrocarbons in excess of air involves the simultaneous formation of carbon dioxide and water; no selective oxidation takes place, but oxidation is complete even though a considerable portion of the hydrocarbon may escape unchanged. With insufficient air supply, the carbon dioxide may be partly replaced by carbon monoxide. (8) As regards oxidizing power, the metals experimented with may be arranged in the following order, beginning with the most active: osmium, palladium, platinum, ruthenium, iridium, rubidium and gold. (9) At a bright red heat, with excess of air, palladium asbestos causes oxidation of all hydrocarbons as efficiently as does ignited oxide of copper. (10) The

proportion of finely divided metal used upon the asbestos seems to be immaterial, palladium asbestos containing 2 per cent of palladium being nearly as efficient as that containing 80 per cent. In the case of benzene oxidation was observed to commence at 250° C.

The discovery of the catalytic action of metallic oxides in accelerating the process of the oxidation of methane was announced in 1906 by Sabatier and Mailhe.[45] Their experiments were performed in the presence of copper oxide, under conditions which resulted in the formation of liquid products containing small quantities of formaldehyde and formic acid. Analogous results were obtained by substituting for copper oxide, the oxides of cobalt or nickel and for methane, other members of the saturated series of hydrocarbons. It was found that the metallic oxide catalyst contained in a glass tube become incandescent at the point where the gas mixture impinged upon it when first heated to about 200° C., and remained incandescent in the stream without further external heating. The paraffins from methane to heptane behaved in the same way and oxidized completely except for the trace of aldehydes and acids. These researches were followed by a relatively large number of investigations undertaken in the presence of different catalysts and under a variety of conditions but accounts of only a few of these are to be found in the general literature, the majority being covered by patents.

The poor progress that had been made in the utilization of natural gas despite the enormous waste then occurring and the need for cheap formaldehyde was emphasized by Wöhler [46] in 1912. In tests which he described, the oxidation of methane by passing it over nickel or silver gauze at 500° to 550° C. gave only small percentages of formaldehyde. The use of higher temperatures resulted only in failure. He attributed this failure to the fact that at these temperatures, methanol, the primary oxidation product, decomposed very rapidly, while at lower temperatures its velocity of formation was too low for the process to be of any value.

Oxidation in the presence of mild catalysts such as pumice or ferric oxide and at low temperatures [17b] results in the acceleration of the oxidation and decomposition of the intermediate products to a greater extent than the oxidation of the hydrocarbons themselves. At high temperatures the rate of decomposition is so increased that only hydrogen and oxides of carbon are formed. Notwithstanding that the oxides of copper and nickel have been found to be too violent, they are much less so than the metals themselves. Even surface effects alone such as are produced by charcoal, pumice, brick, etc., are such that if appreciable decomposition of the hydrocarbon is to be effected, only small efficiencies toward formation of valuable compounds are obtained.[47]

The relative effectiveness of some of the various catalysts which have

[45] Sabatier and Mailhe, *Compt. rend.* **142**, 1394-95 (1906).
[46] Wöhler, "Herzog's Chem. Tech. der Organischen Verbindungen," Heidelberg, Winter, 1912, p. 558.
[47] *See also* Layng and Soukup, *Ind. Eng. Chem.* **20**, 1052 (1928).

been suggested may be deduced from the temperatures necessary to use before they become active toward the oxidation reaction. Reyerson and Swearingen [48] found that metallic catalysts deposited on silica gel resulted only in the complete oxidation of methane to water and carbon dioxide. With copper the reaction started at 200° C., with platinum at 240° C., and with palladium at 330° C. With a catalyst of molybdenum oxides produced by partial reduction of molybdenum trioxide, oxidation of methane to formaldehyde is very faint at 300° C., noticeable at 400° C., measurable at 500° C., is very active at 550° C. with moderate gas velocities and extremely active at 600° to 700° C. even at high gas rates.[49] Without a catalyst a time of contact of 0.067 second at 1000° C. is used to oxidize methane to formaldehyde with a 16 per cent methane, 84 per cent air mixture.[50]

The presence of a catalyst does not seem to change the course of the reaction between methane and oxygen, but apparently influences the rates of the various steps.[51] Silver on pumice prepared by ignition of the nitrate followed by reduction at 500° C. become active as an oxidation catalyst at about 320° C. and gave complete reaction at 610° C. The presence of hydrogen with the formaldehyde indicated decomposition of this intermediate. Copper catalysts prepared in a similar way with reduction at 400° C. become active at about the same temperature but were not as violent, requiring somewhat higher temperatures for complete reaction. A vanadium oxide catalyst supported on pumice and prepared from ammonium vanadate did not become active until a temperature of 480° C. was reached. However, it gave complete consumption of oxygen from the 2 to 1 methane-oxygen mixture at 580° C. Asbestos platinized from ammonium chloroplatinate become active at 430° C. On the other hand, platinum black reduced on asbestos by formaldehyde induced reaction at room temperature. The only oxygenated intermediate found in these experiments was formaldehyde, aside from a small amount of acetic acid detected in the wash water from the copper catalyst experiments.[52]

When the ratio of air to methane becomes very high, as in mine gases which contain about 4 per cent methane, platinum black is no longer the violently active catalyst for the oxidation it is in mixtures rich in hydrocarbon.[53] The oxide type of catalysts, however, become very efficient in the temperature range of 150° to 350° C. in catalyzing the oxidation of the methane. Cobalt oxide was found to be the most effective catalyst, with manganese and nickel oxides next in order.

The reactions between oxygen and hydrocarbons are strongly exothermic and unless the heat of reaction is removed from the reaction zone

[48] Reyerson and Swearingen. *J. Phys. Chem.* **32**, 192-201 (1928).
[49] U.S. Pat. 1,675,029 (1928) James assr. to Byrnes.
[50] Ger. Pat. 497,694 (1924) Roelen.
[51] Campbell, *J. Soc. Chem. Ind.* **48**, 93-7T (1929).
[52] The production of acetic acid and acetaldehyde from mixtures of methane and hydrogen plus oxygen by passage over catalysts having both oxidizing and reducing power such as tin, silver, or mercury vanadates has been claimed. Brit. Pat. 304,855 (1927) I. G. Farbenind.
[53] Yant and Hawk, *J. Am. Chem. Soc.* **49**, 1454-60 (1927).

by some means, the temperature becomes so high as to cause complete oxidation. The use of diluents either in the form of excess air, hydrocarbon, water vapor, or non-reacting gaseous substances has been proposed either empirically or with the specific object in view. Thus methane with a large excess of air is heated to 150° to 200° C. in the presence of metals or metallic couples.[54] In practice a mixture of 3 parts of methane mixed with 100 parts of moist air is passed over copper, silver, or both to convert part of the methane to formaldehyde. The chief difficulty of this method of heat control lies in the recovery of the formaldehyde from the extremely dilute exit gases from the reaction. Scrubbing with water to give dilute "formalin" solutions is necessarily resorted to.

Numerous materials have been tried and patented for use as catalyst for the oxidation of methane and other aliphatic hydrocarbons of the same homologous series to form oxygenated products. Among these may be mentioned: tan bark,[55] fatty substances,[56] Werner's salts,[57] molten metal,[58] titanium compounds,[59] copper,[54] ignited silver or copper cyanamide,[60] silver in metallic couples,[61] cobalt nitrate,[62] copper oxide, iron oxide, manganese dioxide, barium dioxide,[62] platinum, porous asbestos,[7] vanadium dioxide,[63] thorium oxide, cobalt oxide, uranium oxide,[64] gold, platinum, manganic oxide, nickelous oxide, aluminium oxide, cupric oxide, silver oxide, lead monoxide, cerium dioxide,[65] high melting point electronegative low atomic volume metals as molybdenum, vanadium, manganese, tungsten, uranium, chromium, titanium, zirconium, and thorium oxides and compounds,[66] activated copper suboxide,[27] burnt clay, etc., impregnated with boric or phosphoric acids,[67] phosphates and borates of tin,[68] vitreous material,[69] silica gel metallized with platinum, palladium, copper and silver,[48] metallic oxides,[58] oxides of alkaline earth metals,[70] pulverized silica gel containing platinum, iron, copper, or nickel,[71] chromium hydroxide gel containing salts or oxides of silver, magnesium, zinc, cadmium, lead, calcium, nickel, cobalt, manganese.[72]

Under experimental conditions some exceptionally high yields have been obtained. Thus Medvedev [65] in studying a number of catalysts under carefully controlled conditions was able to convert over 50 per cent of

[54] Ger. Pat. 286,731 (1913) Verein. für Chem. Ind. Mainz.
[55] U.S. Pat. 891,753 (1908) von Unruh.
[56] Ger. Pat. 214,155 (1909) Sauerstoff u. Stickstoff Ind.
[57] Ger. Pat. 307,380 (1916) Müller.
[58] Brit. Pat. 176,438 (1922) Therm. Ind. and Chem. Research Co.
[59] Brit. Pat. 182,843 (1921) Atack.
[60] Brit. Pat. 163,046 (1920) Clancy assr. to Nitrogen Corpn.
[61] Ger. Pat. 286,737 (1913).
[62] Ger. Pat. 207,380 (1907).
[63] a. French Pat. 515,685 (1920) Selden Co.; b. Brit. Pat. 170,022 (1921) Selden Co.; c. Ger. Pat. 347,610 (1916) Wohle.
[64] Elworthy, *Roy. Soc. Canada* 16, 93 (1922)
[65] Medvedev, *Trans. Karpov. Inst. Chem.* 3, 54-65 (1924).
[66] U. S. Pat. 1,588,836 (1926) James; U. S. Pat. 1,675,029 (1928) James.
[67] U.S. Pat. 1,487,020 (1924) Mittasch, Willfroth and Balz; Brit. Pat. 199,886 (1922) Badische Anilin und Soda Fabrik.
[68] Medvedev, *Trans. Karpov. Inst. Chem.* 4, 117-25 (1925).
[69] U. S. Pat. 1,729,711 (1929) Curme to Carbide and Carbon Chem. Co.
[70] Brit. Pat. 174,642 and 174,643, Winternitz, Bullinger, and Tüchner.
[71] Brit. Pat. 304,269 (1927) Silica Gel Corpn.
[72] Fr. Pat. 659,644 (1929) National Processes Ltd.

the reacting methane to formaldehyde. The conditions of his best results were: a mixture containing 13.8 per cent methane, and 17.98 per cent oxygen passed through the tube at 600° C. at a velocity of 0.23 liters per minute with 5.02 per cent of the methane going to formaldehyde while a total of 8.65 per cent of methane reacted to give 58.04 per cent of the reacting methane going to formaldehyde. From a study of the activity of the different catalysts at different temperatures this investigator was led to the conclusion that all of the oxidation reactions were accelerated by the catalysts thus showing their non-specific nature. The catalysts used were: gold, platinum, and oxides of manganese, nickel, aluminum, copper, silver, lead, and cerium on asbestos supports. Manganese oxide was the most active of these catalysts and copper oxide the least active. Glass at 600° C. gave the best yields of formaldehyde, possibly because of less activity toward decomposition of the aldehyde. By passing methane with steam and air over copper or silver heated to 500° C. Schönfelder [73] found that 55 to 58 per cent of the hydrocarbon was oxidized to formaldehyde and 10 to 20 per cent to carbon monoxide, carbon dioxide, and water, while 25 to 40 per cent remained unchanged. Blair and Wheeler [11] in studying the effect of temperature upon the rate of the reaction of methane and oxygen without a catalyst obtained a 65 per cent conversion into formaldehyde under optimum conditions in a circulation method. However, the yield of valuable products in all of these cases has been too small to warrant application of the processes to commercial practice.

Lind and Bardwell [74] have summarized the effects of radio-active materials on methane oxidation. Under the influence of the alpha radiation from radon the oxidation of methane proceeded completely to carbon dioxide and water. The oxidation took place in one step, and from the numerical relation between the number of gaseous ions produced and the methane molecules oxidized, the formation of triplet ion clusters was postulated as shown:

$$(O_2.CH_4O_2) + O_2^-.CH_4O_2) = 2CO_2 + 4H_2O.$$
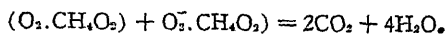
As much as 75 per cent of the theoretical oxidation based on the radiation was obtained. Selenium diethyl was found to accelerate the oxidation under the influence of alpha radiation from radon.

In preparing formaldehyde from methane on a commercial scale it is beneficial that oxygen instead of air be used to prevent the undue dilution of products and to prevent the interference of diluents with the reaction at temperatures giving good yields. Ledbury and Blair [75] have proposed conditions for commercial operation to form one ton of formalin per day. A mixture having an initial composition of 80 per cent methane and 20 per cent oxygen is passed through a heating zone at 700° C. with a time

[73] Schönfelder, *Ber. ges. Kohlentech.* 4, 247-63 (1923); *Chem. Zentr.* 1923, IV, 206-7; *J. Chem. Soc.* 124, 1175 (1923).
[74] Lind and Bardwell, *Science* 62, 422-24 (1925); *J. Am. Chem. Soc.* 48, 2347-51 (1926); *Ind. Eng. Chem.* 19, 231-33 (1927).

of contact of one second and formaldehyde scrubbed from the exit gas. It is estimated that 30 per cent recovery of methane as formaldehyde could be accomplished. The cost of operation is estimated at $180 per ton of formalin exclusive of the cost of methane. The authors were forced to conclude that the industrial oxidation of methane for the manufacture of formalin could only be considered as economically feasible if methane could be obtained in large quantities at a very low cost. It does not appear that there is any immediate likelihood of the formaldehyde produced in this way competing with that produced from coal through the intermediate agency of water gas and methanol. Without doubt more efficient methods for the atmospheric pressure oxidation of methane will be devised. Nash and Stanley [76] are confident that a process for the manufacture of formaldehyde from methane, which is capable of competing with the existing methanol oxidation process, will be perfected. A natural gas containing 93 per cent methane, 3.5 per cent ethane, and 3 per cent nitrogen has been successfully converted to hydrogen and carbon monoxide and the formation of formaldehyde by this means may succeed where direct oxidation is out of the question.[77]

Oxidation with Metallic Oxides

The oxidation of methane by copper oxide to form carbon dioxide and water is a common analytical procedure. With copper oxide alone this oxidation starts at about 550° C. and at moderate rates of flow (2.4 to 3 minutes time of contact) requires a temperature of over 700° C. for completion.[78] A copper oxide containing 13.8 per cent of cuprous chloride suspended on it, is much more active, however, and in the range of 400° to 470° C. with about 4 minute times of contact oxidation is complete. Additions of 2 per cent of the oxides of either vanadium, nickel, cobalt, or manganese caused an activation of the copper oxide. Good balances were obtained which indicated that all of the methane reacting formed carbon dioxide and water and that intermediate oxidation products did not persist. Under less severe conditions, i.e., shorter times of contact or lower temperatures, it is possible that intermediate oxidation products may be obtained.

Under certain conditions methane reduces metallic oxides and is itself oxidized to methanol or formaldehyde.[79] Blackmore [80] claimed a yield of 125 pounds of methanol from 1500 cu. ft. of methane at 127° C. while at 157° C., 118 pounds of formaldehyde were produced. The oxides used were ferrous-ferric oxide, cupric oxide, manganese, and barium oxides. These yields are practically theoretical and if the process actually gave such yields economically, it would possibly have been in operation long

[76] Nash and Stanley, *Fuel* 7, No. 9, 397-401 (1928).
[77] Boomer, *9th Annual Rept. Sci. Ind. Res. Council Alberta*, 1928, 51-3; *compare* Chapter IX.
[78] Campbell and Gray, *J. Soc. Chem. Ind.* 49, 447-53T, 1930.
[79] Mueller, *Bull. soc. chim.* 2, 440-1 (1864); *Ann. phys.* 122, 139 (1864).
[80] U. S. Pat. 774,824 (1904) Blackmore.

ago, notwithstanding that batch operation would probably be required. The following reactions are said to occur when the oxide is kept at the temperature of 125° and 160° C., respectively:

$$4CH_4 + Fe_3O_4 = 3Fe + 4CH_3OH$$
$$2CH_4 + Fe_3O_4 = 2Fe + 2H_2O + 2H_2CO.$$
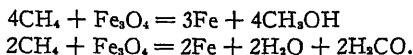
By passing gases from the distillation of coal under a pressure of 400 atmospheres over metallic oxides, such as ferric oxide, at a temperature of 300° to 600° C., it is claimed that alcohols may be obtained.[81a] However, by using methane or gases containing methane in a similar manner only higher hydrocarbons are formed.[81b]

The oxidation of methane to hydrogen and carbon monoxide by passage over the oxides of metals capable of existing in several degrees of oxidation has been claimed.[82] The use of TiO_2 and CrO_3 for this purpose is specified.

Claims have also been made for the conversion of hydrocarbons in the gaseous phase into other compounds by passage over a copper suboxide at temperatures ranging from 250° to 800° C.[83] No information is available in the general technical literature regarding conversions or yields obtainable by processes similar to those disclosed in the patent literature.

It is difficult to determine thermodynamically the possibility of the occurrence of such reactions as have been claimed because of lack of data in regard to the metallic oxides. However, some data are available and will be used here.

The free energy decreases as functions of temperature for the formation of zinc oxide,[84] mercuric oxide,[85a] and silver oxide[85b] from the elements have been determined. By combining these values with the free energy decreases attending the formation of methanol[86] and of methane[87] from the elements, the free energy decrease for the reaction typified by the following with zinc oxide:

$$CH_4 + ZnO(solid) = Zn(solid) + CH_3OH(gas)$$
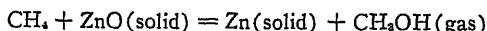
may be obtained. Then by means of the relation, $RT \ln K = -\Delta F$, it is possible to determine the values at different temperatures for

$$K = \frac{p_{CH_3OH}}{p_{CH_4}}.$$

Values for log K are shown in Figure 11 as functions of temperature.

The values of K for the reduction of zinc oxide by methane to form methanol are extremely unfavorable even at temperatures of 727° C. The

[81] a. Brit. Pat. 255,828 (1925) Compagnie de Bethune; b. Brit. Pat. 255,829 (1925) Compagnie de Bethune.
[82] Ger. Pat. 525,556 (1929) Wilke and Fried assrs. to I. G. Farbenind.
[83] U. S. Pat. 1,672,081 (1928) Nielson.
[84] Maier and Ralston, *J. Am. Chem. Soc.* 48, 371 (1926).
[85] a. Lewis and Randall, "Thermodynamics," New York, McGraw-Hill Book Co., 1923, p. 484; b. Lewis and Randall, *ibid.*, p. 481.
[86] Francis. *Ind. Eng. Chem.* 20, 283 (1928).

values of log K for this reaction are not shown in Figure 11. Determination of K for the reaction with silver oxide leading to reduction to silver shows this reaction to be favorable for the formation of methanol. Calculation of K for the reduction of mercuric oxide by methane to give methanol is favorable and less affected by temperature.

Free energy values for various copper compounds have recently been critically reviewed and collected by Randall, Nielsen, and West.[88] The proper values from this compilation have been used in calculating the equilibrium conditions for the reactions:

$$CH_4(g) + 2CuO(s) = Cu_2O(s) + CH_3OH(g) \qquad (d)$$
$$CH_4(g) + CuO(s) = Cu(s) + CH_3OH(g) \qquad (e)$$
$$CH_4(g) + Cu_2O(s) = 2Cu(s) + CH_3OH(g) \qquad (f)$$
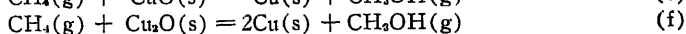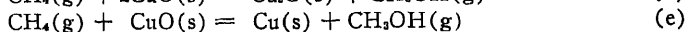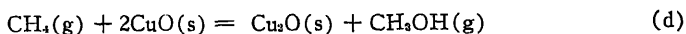
The values of log K as a function of temperature for these reactions are shown by lines 3, 4, and 5 in Figure 11.
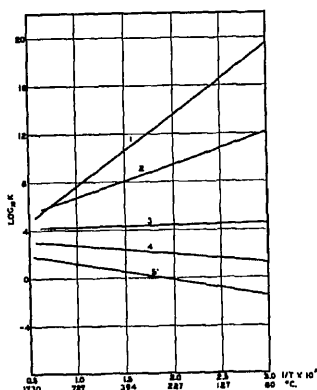
FIG. 11.—Equilibrium as a function of temperature for the following reactions:
1. $CH_4(g) + Ag_2O(s) = CH_3OH(g) + 2Ag(s)$
2. $CH_4(g) + HgO(s) = CH_3OH(g) + Hg(l)$
3. $CH_4(g) + 2CuO(s) = CH_3OH(g) + Cu_2O(s)$
4. $CH_4(g) + CuO(s) = CH_3OH(g) + Cu(s)$
5. $CH_4(g) + Cu_2O(s) = CH_3OH(g) + 2Cu(s)$
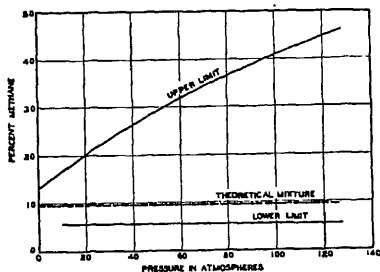
FIG. 12.—Effect of initial pressure on inflammability limits of methane-air mixtures. Data of Bone and Newitt.[96] [Compare Berl and Werner, Z. angew. Chem. 40, 245-50 (1927).]

The free energies of formation and heats of formation for the oxides of lead are given by Millar[89] as shown in Table X. The specific heat of methane is given as $C_p = 7.5 + 0.005T$,[85]

TABLE X.—Free Energy and Heats of Formation of Some Lead Oxides.

Substance	$\Delta F°_{298}$ of Formation	ΔH_{298} (Formation) from ΔF and S
PbO (red)	− 45,050	− 52,360
Pb₃O₄	− 147,270	− 172,440
PbO₂	− 52,010	− 65,960

[88] Randall, Nielsen, and West, Ind. Eng. Chem. 23, 388-400 (1931).
[89] Millar, J. Am. Chem. Soc. 51, 207-14 (1929).

the heat of formation of methane as $\Delta H_{298} = -16,963$ by Randall and Gerard, and the specific heat and heat of formation of methanol as

$$CH_3OH; \quad C_p = 0.6 + 0.0335T \ [86]$$
$$\Delta H_{298} = -51,050.$$

Using these values and the specific heats for the different metals and oxides as given in the "International Critical Tables" [90] it is possible to calculate the free energy change as a function of temperature and the equilibrium constants for the reactions:

$$CH_4 + PbO = Pb + CH_3OH \tag{g}$$
$$CH_4 + PbO_2 = PbO + CH_3OH \tag{h}$$
$$4CH_4 + Pb_3O_4 = 3Pb + 4CH_3OH. \tag{i}$$
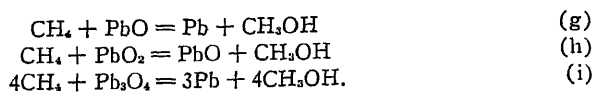
Reaction (h) is favorable and reactions (g) and (i) so unfavorable as not to warrant plotting.

Thermodynamic data on the iron oxides are not directly available but calculations based on free energy values determined from equilibrium data between steam and iron and from specific heat data at low temperatures by the entropy principle [91] show that the formation of methanol by the reactions shown is very unfavorable.

$$CH_4 + Fe_3O_4 = 3FeO + CH_3OH \quad \text{(unfavorable)} \tag{j}$$
$$CH_4 + FeO = Fe + CH_3OH \quad \text{(unfavorable)} \tag{k}$$
$$4CH_4 + Fe_3O_4 = 3Fe + 4CH_3OH \quad \text{(very unfavorable)} \tag{l}$$
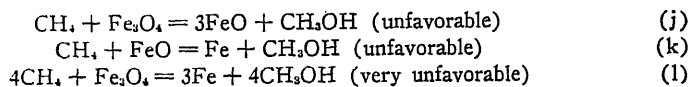
Unless the equilibrium constants for a reaction is about 1 or its $\log_{10}$ about 0 at temperatures of 300° to 500° C. for these reactions, the possibility of forming methanol is very slight. Thus reaction of methane with metallic oxides to form methanol appears to be favorable only in the case of copper, mercury, or silver oxides. Even with these compounds the reaction to form carbon dioxide and water, complete combustion, is so much more favorable than the formation of alcohol or aldehyde, that there seems but little hope of utilizing methane in this way. The relatively much larger energy changes involved in the formation of water and carbon dioxide makes it very difficult to stop any oxidation process short of complete combustion. Control of the rates of the different reactions seems to offer the only chance of forming methanol.

Under suitable conditions, methane may be used to reduce the oxides of such important elements as sulfur, iron and zinc to the elemental state. Such reductions are dependent upon catalytic effects such as are obtained in heterogeneous systems and to be useful in metallurgical processes require commercial units especially designed to suit the peculiarities of methane.* The facts that reduction of certain oxides with methane is thermodynami-

[90] International Critical Tables, New York, McGraw-Hill Book Co., Vol. V, p. 95 (1929).
[91] The entropies, S_{298}^0, for iron oxides are given as FeO = 12.7 ± 2.0, Fe₃O₄ = 34.69 ± 0.2; Millar, *J. Am. Chem. Soc.* 51, 215-22 (1929).
* Maier, U. S. Bureau of Mines, reported before Pet. Div., Am. Chem. Soc., Buffalo, Sept. 1, 2, 1931.

cally possible and that the rates of reaction become appreciable at temperatures slightly higher than 800° C. have led to the consideration of methane as a metallurgical reagent and a number of experimental projects are now in progress at smelting and chemical plants.

Oxidation under Pressure

In considering the pressure oxidation of hydrocarbons with oxygen to form alcohols and aldehydes, it will be well to review some of the phenomena connected with the non-catalytic combustion of hydrocarbons under pressure, since the literature regarding the oxidation to form oxygenated products is very meager.[92]

The effect of pressure upon the limits of inflammability of saturated gaseous hydrocarbons is similar to that shown by Figure 12 for methane.

From this data it may be seen that a mixture of say, 20 per cent methane and 80 per cent air would be too rich to burn at atmospheric pressure; would burn with a slow and cool flame at about 25 atmospheres pressure; and would explode at higher pressures. Increase in pressure is, hence, equivalent to using a mixture more dilute in methane, as far as obtaining explosions is concerned. In general, the lower the oxygen concentration in a hydrocarbon mixture or the lower the initial temperature, the higher will be the pressure required for the ignition of the mixture, and conversely the higher the pressure or temperature of the initial mixture, the lower will be the oxygen concentration necessary for combustion. Spontaneous reaction begins at temperatures above 400° C. In explosions at high pressures the oxygen is not completely consumed.[93, 94]

Methods proposed for the partial oxidation of hydrocarbons under pressure to form oxygenated compounds recommend the use of low oxygen concentrations to avoid the hazard of explosions from mixtures already under considerable pressure. Also the extent of reaction in a given quantity of mixture must be limited since the large quantities of heat evolved in the oxidation would tend to raise the temperature to a dangerous extent. The excess hydrocarbon gas serves to absorb the heat of reaction as sensible heat which may be removed in a separate apparatus. The introduction or abstraction of considerable quantities of heat from high pressure equipment is a difficult undertaking and is avoided whenever economically possible by limiting the extent of the endothermic or exothermic reaction occurring.

In studying the combustion of liquid and solid fuels in air at pressures from 0.3 to 4 atmospheres, Frankland[95] found that the candle power of wax candle flames varied almost linearly with pressure, falling off 5.1 per

[92] For discussions regarding high pressure equipment and methods *see* a. Maxted, *J. Soc. Chem. Ind.* **45**, No. 22, 366-70 (1926); b. Ernst, Reed and Edwards, *Ind. Eng. Chem.* **17**, 775-88 (1925); c. Ernst, *ibid.* **18**, 644-9 (1926); *J. Soc. Chem. Ind.* **48**, 591 (1929).
[93] *See* Cooper and Wiezevich, *Ind. Eng. Chem.* **21**, 1210-4 (1929).
[94] For an exposition of the phenomena attending non-catalytic gas phase combustions under pressure *see* Bone, Newitt, and Townend, "Gaseous Combustion at High Pressures" London, Longmans, Green & Co., Ltd., 1929.
[95] Frankland, *J. Chem. Soc.* **15**, 137 (1862).

cent for each inch of mercury pressure below atmospheric and becoming zero at the lower pressures, and concluded that combustion under elevated pressure is less perfect and combustion under reduced pressure is more perfect than at atmospheric pressure. Bone and Townend[96] suggest that a hydrocarbon flame should become more luminous in atmospheres under compression but do not support their statement with experimental evidence nor adequate reasons. Franklands' observations have been confirmed qualitatively by Francis[97] with gaseous hydrocarbons at pressures up to 38 atmospheres. However, none of these investigators studied the formation of oxygenated compounds from the hydrocarbons.

Reid[98] recently employed high pressures while attempting the oxidation of heavy hydrocarbons but does not give detailed data. Extensive investigations on the oxidation of paraffin wax under high pressures have been made by Fischer.[99] This work showed iron and copper salts to be the best catalysts and yields as high as 74 per cent of fatty acids were obtained.

By heating methane with excess oxygen, air, or ozonized air at red heat (600° to 1000° C.) under pressure in the presence of porous nonmetallic surfaces as pumice, brick, slag, asbestos, etc., it has been claimed[100] that methanol and formaldehyde may be produced. The products are condensed at atmospheric pressure by a counter current of cold air or gas. The catalyst might also contain substances such as oxides and hydroxides of alkalies or alkaline earths, magnesium or calcium chlorides or copper sulfate which are hydrated at ordinary temperatures but lose water at high temperatures.

Various attempts have been made to obtain formic acid by direct oxidation of methane. Bruktus[101] invented a process for oxidizing methane to formic acid within the cylinder of a power-driven compressor. The hydrocarbon and oxygen, in combining proportions, were introduced into the compressor at such a rate that when the piston had completed two-thirds of its stroke the gases were under a pressure of thirty atmospheres and at a temperature of nearly 500° C. During the remainder of the stroke, air, independently compressed to forty-five atmospheres, was introduced into the cylinder in a finely divided stream to produce a cooling effect and to increase the oxygen content. At the end of the compression stroke the gases were discharged and the formic acid was absorbed by water. The residual gases were recirculated. Unfortunately no data are available as to the yields obtained.

[96] Bone and Townend, "Flame and Combustion in Gases," London, Longmans, Green & Co., Ltd., 1927.
[97] Thesis for Chem. Eng. degree Worcester Polytech. Inst. (1929); Francis, Pet. Div. Am. Chem. Soc., Indianapolis, March 30-April 3, 1931.
[98] Reid, "Oxidation of Heavy Hydrocarbons at high Temperatures and Pressure" at National Symposium of Organic Chemistry at Syracuse, 1925.
[99] Fischer, *Ges. Abhandl. Kenntnis Kohle* 4 (1919).
[100] Ger. Pat. 421,215 (1922) Bakelite Ges. m.b.H. and Hessen.
[101] Brit. Pat. 217,747 (1924) Bruktus.

The conversion of methane into formaldehyde, ethylene, and higher hydrocarbons by a process of oxidation has been claimed.[102] A mixture of air and methane is heated in the presence of a copper gauze catalyst under pressure to give formaldehyde, which by reaction with methane forms ethylene with removal of water in the presence of catalysts of iron, cobalt, nickel, chromium, vanadium, etc., at 500° C.—and under extremely high pressures.

The partial oxidation of natural gas on a commercial scale by the Empire Refining Co. to form a mixture of oxygenated hydrocarbon compounds has created considerable interest.[103a] It has been reported that 70,000 gallons of a mixture comprising methanol, formaldehyde, and acetaldehyde have been produced daily by the company's process.[103b] This mixture of oxygenated compounds is formed during the process of removing very small proportions of oxygen (air) from natural gas prior to transmission through long pipe lines. The removal of oxygen from the hydrocarbon gas by reacting it with a portion of the hydrocarbon material is done to prevent inside corrosion of the pipe line by attack of oxygen on the steel. The oxidation step is conducted on the outlet side of compressor stations and is consequently accomplished, at that point, under a line pressure that may vary according to the length of the transmission line or location of the station and may average between 300 to 450 pounds per square inch. However, the efficiency of the oxidation step to form useful products is not affected by the operation at somewhat lower or considerably higher pressures.* The process is of interest since it represents a by-product production and hence, should be capable of yielding a product to compete in cost with formaldehyde and methanol made by the usual methods. It is certainly indicative of what may be expected in the way of natural gas utilization by oxidation processes.

The mixed product obtained may be marketed as such or may be treated by such means as distillation and scrubbing to separate into the different components. It is also possible that by treating such a mixture with phenol, resins will be formed which may then be separated from the methanol and used for molding or other purposes.

Bone [104] has recently claimed that Newitt and Haffner working in his laboratory have been able to obtain methanol by the direct oxidation of methane at 360° C. and 100 atmospheres pressure. With a mixture of methane and oxygen in the ratio 9 to 1 reaction was complete in a few minutes under these conditions. The results showed that 17 per cent of the reacting methane formed methanol, 0.6 per cent formaldehyde, and the rest water and oxides of carbon. Hydrogen was not formed and no peroxide was detected. Such results, obtained by a process of slow oxidation in the absence of catalysts and at fairly low temperatures, when com-

[102] French Pat. 637,050 (1926) Spindler.
[103] a. Brooks, *J. Inst. Pet. Tech.* 24, 744 (1928); b. Burrell, *Natl. Petroleum News* 22, No. 22, 80 (1930).
* Personal communication from Dr. S. P. Burke.
[104] Bone, *Nature*, March 28, 1931, p. 481.

pared to results obtained at atmospheric pressure, show the remarkable influence of pressure on the reaction.

Several patents have recently appeared claiming the formation of oxygenated products by the catalytic, high pressure, vapor phase oxidation of normally gaseous hydrocarbons and of hydrocarbons up to six carbon atoms in length. In these processes [105a] the mixture of air and hydrocarbon vapor is passed over suitable catalysts at temperatures determined in advance by the character of the catalyst used. The reaction temperature used is ordinarily between the approximate limits of 200° and 600° C. and preferably approaches the lower limit of the range for the higher hydrocarbons. The pressure of operation may range from a minimum of 200 pounds per square inch to a preferable range of 1500 to 3500 pounds per square inch. It is particularly interesting to note the low concentrations of oxygen which are mentioned as desirable in contrast to the excess oxygen that is used in the oxidation of the aromatic hydrocarbons at atmospheric pressures. Fifteen per cent of oxygen is claimed as the maximum desirable concentration and concentrations as low or lower than 5 per cent are desirable in certain cases. A mixture of one gram atom of oxygen per gram mol of hydrocarbon has been claimed.[105e] The hydrocarbon may be preheated to a point short of reaction temperature and then the oxygen passed in, the heat of reaction of the oxygen and hydrocarbon being sufficient to bring the mixture to the proper temperature for the desired reaction.[105a]

There are several obvious objections to this method of introducing the oxygen into the hydrocarbon gas. The most important of these is that by so introducing the oxygen a very high concentration of oxygen is obtained at the point of entry which may quite easily result in the complete combustion of considerable amounts of the preheated hydrocarbons to form carbon dioxide and water rather than the incomplete combustion products desired. The whole purpose of the low oxygen concentration is thereby defeated. Another objection is the hazard of explosions caused by the formation of explosive mixtures during the mixing.

Young [105d] has overcome these objections by passing a relatively cool mixture of hydrocarbon and oxygen into the reaction zone, and then forcing heated hydrocarbon into the reaction zone to raise the temperature of the whole to a point where reaction takes place. The solution of oxygen in hydrocarbon obtained by saturating the hydrocarbon with oxygen under pressure to the limit of solubility under the conditions maintained in the saturator, may be preheated to a temperature of about 150° C. but preferably not over 200° C. to avoid reaction, before the reactor is reached.

[105] a. Brit. Pat. 290,613 and b. 295,356 (1927) Walker assr. to Empire Gas and Fuel Co.; c. Brit. Pat. 321,494 (1928) Arnold assr. to Standard Oil Development Co.; d. U. S. Pat. 1,735,486 (1929) Young assr. to Standard Oil Development Co.; e. Can. Pat. 291,411 (1929); U. S. Pat. 1,776,771 (9/30/30) Boomer assr. to Governors of University of Alberta; f. Can. Pat. 289,856 (1929) Lewis and Frolich assr. to Standard Oil Development Co.; g. Can. Pat. 300,567 (1930) Walker assr. to Empire Gas and Fuel Co.; h. French Pat. 682,979 (1929) Standard Oil Development Co.; i. Can. Pat. 300,798 (1929) Walker assr. to Empire Gas and Fuel Co.; j. U. S. Pat. 1,812,714 (June 30, 1931) Pugh, Tauch and Warren assrs. to Standard Oil Development Co.; k. Brit. Pat. 341,130 (1931) Standard Oil Development Co.

Because of the low oxygen concentration possible to use satisfactorily, and the consequent low conversion of hydrocarbon per pass through the reactor it is necessary to recycle the gas. This is done by condensing the liquid products by cooling the reaction mixture through heat interchange with the cold entering mixture and after separation and proper regulation of oxygen content, passing the gases again through the hot catalyst zone. In this way it is possible to obtain high yields of oxidized products, chiefly methanol from methane and methanol, ethanol, and propanol from the higher homologs of methane.

Separation of the oxidized products from unreacted hydrocarbons may be accomplished by distillation but is better accomplished by scrubbing the reacted gases with a mixture of methanol and water which exerts a preferential action in the separation of the hydrocarbons from the oxidized product. Separation of the alcohols from each other in the product from the oxidation of five or six carbon atom hydrocarbons by distillation is practically impossible because of the close boiling ranges of some of the alcohols. Esterification or the use of close "cuts" of the alcohol fraction for solvents as such would necessarily be resorted to.

Among the catalysts which are mentioned for these processes are platinum, palladium, chromium, manganese, iron, copper, nickel, gold, silver, oxides of copper, manganese, iron, nickel, vanadium, chromium, molybdenum, cerium, and other metals forming higher and lower oxides and their mixtures. Catalyst supports of the ordinary type such as pumice, asbestos, or alundum may be used. It is highly questionable whether this formidable array of catalysts has been thoroughly investigated and the probability is that only such catalysts as exert a mild oxidizing action are to be found useful in pressure oxidation. An example of such consists of a mixture of zinc and lead chromates or broadly of mixtures of a salt of a second group metal with a salt of a fourth group metal.[105u] Other combinations have also been claimed, as for instance, copper wire coated with borax, copper wire coated with fused sodium tungstate, copper wire coated with fused borax and sprinkled with iron powder, etc.[105c]

The fact that the oxidation of methane even under high pressure and in the presence of active catalysts requires a temperature of about 500° to 600° C. confirms the conclusion that methane is extremely unreactive and as the lowest member of the paraffin series occupies a unique position. The ease of oxidation to form alcohols increases with the increasing number of carbon atoms in the hydrocarbon. Both lower temperatures and pressures may be used when the higher homologs of methane are acted upon with oxygen to form intermediate oxidation products. The ethane content of hydrocarbon gases comprising methane and ethane may be selectively converted by preheating the hydrocarbon gas at 100 pounds per sq. in. pressure to about 750° F., admixing less than 50 per cent by volume of air, and passing the mixture over a catalyst at about 850° F.[105l]

Catalytic oxidation of the low molecular weight aliphatic hydrocarbons

under high pressures yields results entirely different from those obtained by oxidation at atmospheric pressure as evidenced by the formation of considerable concentrations of alcohols which may even contain the same number of carbon atoms as the parent hydrocarbon. The use of low oxygen concentrations is undoubtedly of great importance in obtaining intermediate oxidation products as a result of these processes, but even low oxygen concentrations are of no avail in the formation of alcohols in atmospheric pressure oxidations of hydrocarbons. The effect of pressure must be looked to for an explanation of the results obtained.

It is known that pressure is effective in lowering the temperature at which certain reactions can be made to occur. It is probable that a similar effect is obtained in high pressure oxidation reactions and that oxidation of a hydrocarbon such as methane or ethane can be induced at a much lower temperature under a pressure of several hundred atmospheres. If a lower temperature can be used, then the tendency for the primary oxidation products to decompose is reduced. Pressure, furthermore, stabilizes these intermediate oxidation products against decomposition since their decomposition almost invariably occurs with an increase in the number of molecules. Pressure may also be effective in preventing the secondary oxidation of the products first formed by reducing the rate of diffusion and thus decreasing the possibility of an encounter between intermediate oxidation product molecules and free oxygen molecules. It is probable, however, that the oxygen is consumed by reaction with hydrocarbon molecules at a very rapid rate because of the excess of hydrocarbon present, a possibility that leaves small room for postulating secondary oxidations.

Besides low oxygen concentrations, high pressures, and low temperatures, short times of contact must be used. This is true because, in all probability, equilibrium conditions are not reached in the processes when alcohols and aldehydes are obtained as products. Advantage must be taken of the apparent fact that the oxidation reactions occur at a higher rate, under the conditions, than do the decomposition reactions involving the intermediate products. By using rapid rates of flow of reacting gases through the heated zone the unstable products may be removed and cooled before they completely decompose. In general contact times of 1 to 2 minutes have been recommended.

In the discussion of the oxidation at atmospheric pressure it was pointed out that in general surfaces and catalysts had been found to be detrimental to the production of methanol and formaldehyde. The results of high pressure oxidation, however, lead to an entirely different conclusion; namely, that good yields, based on the hydrocarbon reacted, of methanol and formaldehyde may be obtained in the presence of metallic and inert surfaces and that the governing factor is not the kind of surface present but the velocity of the reacting gases over the surface (time of contact). Rates of flow of gas over the catalytic surface in excess of 0.20 liters per hour per square centimeter of superficial catalyst surface must

be used under the conditions of operation for proper yields to be obtained.[105f] Catalysts with porous surfaces would, therefore, yield less product than smooth catalysts because of the longer times of contact possible with them.

As was pointed out in the discussion of catalysis mechanism one of the controlling factors in determining the rate of heterogeneous reactions is the rate at which the reacting gases diffuse through an inert film at the catalyst surface. Since the oxidation reaction may be visualized as a surface phenomenon with the reacting gases diffusing through a film of gas on the catalyst surface, the influence of increasing gas velocity would be to decrease the film, speed up the diffusion of gases to the catalyst, and hence accelerate the oxidation reaction. At the same time the high velocity of the reacting gases would decrease the actual time of contact with the surface and would check the complete oxidation of the hydrocarbons to carbon oxides and water. Consequently the surface velocity of the reactants over the catalyst is a critical factor in pressure oxidation processes.*

At the present time insufficient data are available to warrant the postulation of a mechanism for oxidation under pressure. Although it may be that the effect of pressure is simply to stabilize the alcohols formed intermediately according to Bone's theory, there are indications pointing to a change in the mechanism of oxidation as the pressure is increased. That this may very well be so is indicated by the increased luminosity of flames under elevated pressures of oxygen or air and by the fact that some evidences of pressure effects have been noted in the distribution of oxygen between hydrogen and carbon in the products from pressure explosions. Recent studies [106] of methane oxidation under pressures ranging from 12 to 100 atmospheres and at temperatures of 300° to 400° C. in packed and unpacked tubes seem to indicate that the reaction is homogeneous and of the chain type. Increased surface was found to actually decrease the rate of reaction and to increase the concentration of methanol and formaldehyde in the product. In keeping with the various patent claims increased methanol formation was found to result from both an increase in pressure and an increase in the concentration of methane.

It is unfortunate that the general literature does not contain more detailed information regarding this important development. However, the process patents are relatively recent and the whole matter is involved with the earlier basic patents on hydrocarbon oxidation. It is probable that a number of applications are still on file for which no patents have as yet been issued. Escaping, as it has, the attention of academic investigators in the past, the pressure oxidation process has been an industrial development, and the general public will necessarily have to wait for operating details.

Reactions with Ozone

Because of the greater activity of ozone as compared to molecular oxygen, early workers considered that lower temperatures might possibly be used in the production of oxygenated hydrocarbons from methane by its use with consequent less difficulty from excessive oxidation and decomposition. The importance of ozone as an oxidizing agent was first indicated by Schönbein [107] in 1868.

The first workers found that at ordinary temperatures ozone did not react with methane [108] to form the desired products. Later workers found that at temperatures in the neighborhood of 100° C. noticeable reaction took place and that even at temperatures as low as 15° C. some reaction occurred.[100] However, none of the reported results showed more than traces of methanol. At temperatures of about 100° C. the product was found to contain formaldehyde and formic acid. It was found that at low temperatures ozone could be made to react with methane under the influence of silent electric discharges.[110]

Drugman [111] in repeating the work of Otto found that in general saturated hydrocarbons may be oxidized in the presence of ozone at low temperatures. The primary products may be assumed to be alcohols but these are not present among the final products of the oxidation because of the fact that they rapidly undergo further oxidation to give the corresponding and relatively stable aldehydes, the latter oxidizing, much more slowly to give acids. In the case of methane, for example, it was impossible to detect the presence of even traces of methanol among the reaction products.

Wheeler and Blair [112] passed a mixture containing three per cent of methane in oxygen through an ozonizer and then through a glass reaction tube maintained at various temperatures. This concentration of hydrocarbon was rather low but good interaction was obtained at temperatures above 100° C. as shown in the table of their results. This investigation served to show that relatively small quantities of formaldehyde could be

TABLE XI.—*Oxidation of Methane by Ozone.*

Mixture: 97 per cent oxygen, 3 per cent methane.

Temperature of reaction tube...	15° C.	100° C.	200° C.	300° C.	400° C.
Conversion of methane to HCHO as per cent		9	14	20	9
Ozone reacting as per cent of original	5	53	76	68	52
Ozone directly decomposed as per cent of original..............	Nil	15	15	32	48
Total ozone destroyed, per cent	5	68	100	100	100

[107] Schönbein, *J. prakt. Chem.* 105, 230 (1868).
[108] a. Hauzeau and Renard, *Compt. rend.* 76, 572-4 (1873); b. Maguenne, *Bull. soc. chim.* (2), 37, 298-300 (1882).
[109] a. Mailfert, *Compt. rend.* 94, 1186-7 (1882); b. Otto, *Ann. chim. phys.* (7), 13, 109-16 (1898).
[110] Elworthy, *Trans. Roy. Soc. (Canada)* III, 16, 93-104 (1922).
[111] Drugman, *J. Chem. Soc.* 89, 939-45 (1906).
[112] *J. Soc. Chem. Ind.* 41, 331-2T (1922).

obtained in this way. The heating time of 2.5 minutes, however, was probably too long at the higher temperatures. Experiments with mixtures containing over 60 per cent methane gave similar results. At all temperatures most of the methane was obtained as carbon dioxide with no formation of carbon monoxide. This is probably due to the fact that formaldehyde is oxidized to formic acid and then to carbonic acid at as high a rate as the methane is oxidized to formaldehyde with the result that the formaldehyde concentration is never permitted to build up to such a point where active decomposition would occur. Oxides of nickel, aluminum, iron, etc., deposited on pumice, or platinized asbestos accelerate the decomposition of ozone at temperatures even lower than 100° C. so that very little methane is oxidized under the conditions necessary to use. Ignited pumice alone was not a catalyst.

In attempting to increase the yields of formaldehyde by stabilizing it as hexamethylene-tetramine through interaction with ammonia added to the reaction mixture, these workers found that the effect on formaldehyde yield was insignificant. The yield of formic acid, however, was increased to an amount equal to that of the formaldehyde. The lack of methanol production in these experiments is attributed to the greater ease with which methanol is oxidized compared with methane. Methanol is probably formed as a first step and has but a momentary existence under the experimental conditions.

Urbain [113] had previously found that very little interaction occurred at concentrations of methane as low as one per cent in ozonized air at room temperature, a result substantiated by the later work.

Kloppenburg [114] has emphasized the importance of conducting methane oxidation at the lowest possible temperature, because of the fact that in the presence of metal catalysts, as for example, copper the following relations were found to hold: (a) the most favorable temperature at which oxidation of methane to methanol occurs is at about 600° C.; (b) for the oxidation of methanol to formaldehyde, however, a temperature of only about 300° C. is required; (c) and at 600° C. the velocity of decomposition of formaldehyde to carbon oxides, hydrogen, and water has the effect of lessening to a very considerable extent the actual yields of the desired product. In the presence of cocoanut charcoal and under the influence of silent electric discharges the oxidation of methane by air occurs at 35° C. or lower to form methanol and formaldehyde. It is interesting to note that this patent suggests the revival and extension of the claims made in an earlier patent [115] in which bark was used as the catalyst and the reaction supposedly occurred at temperatures of about 50° C.

The use of metallic oxide catalysts under comparable conditions has also been patented.[116] The formation of formaldehyde is claimed by the

[113] Urbain, *Compt. rend.* **132**, 334-6 (1901).
[114] U. S. Pat. 1,500,080 (1924) Kloppenburg.
[115] Ger. Pat. 214,155 (1909) Sauerstoff u. Stickstoff Ind.
[116] Fr. Pat. 684,969 (1930); Brit. Pat. 343,461 (1929) Gutehoffnungshütte Oberhausen.

passage of air and methane through tubes containing silver or copper oxide catalysts and under the influence of a high tension (80,000 to 90,000 volts) and a high frequency (400,000 cycles) electric field. Yields of 350 to 480 grams of formaldehyde per cubic meter of methane are claimed for this process. This corresponds to a conversion of methane of from 26 to 36 per cent.

An industrial process for the production of formaldehyde by the ozonization of methane, however, apparently has little prospect of success, because of the low yields of formaldehyde obtainable, compared with the
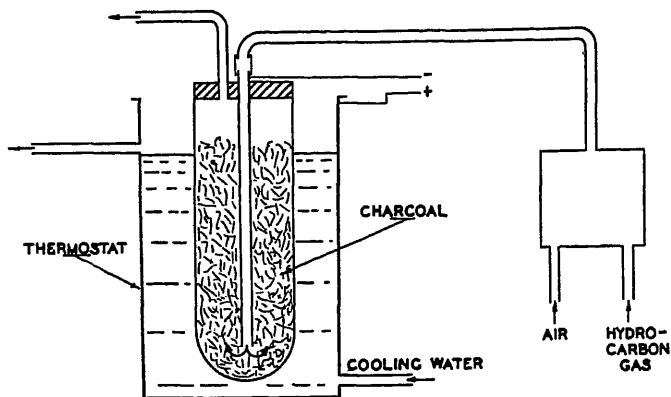
Fig. 13.—Apparatus for the oxidation of methane under the influence of silent electric discharges.

large amount of ozone consumed. A process operated at room temperature, by which methane and oxygen (air) mixtures are passed through an ozonizer in such a way that ozone is formed or starts to form in the presence of methane has but a limited utility because of the low efficiency at which electric energy is consumed in such an apparatus. However, the only partial oxidation found by Elworthy [110] to give promise of commercial value was the action of the silent electric discharge on mixtures of natural gas and oxygen. A product in the form of viscous liquid, containing methanol, formaldehyde, formic acid, polymerized aldehydes, and resins was obtained. The results are partly explainable on the basis of ozone formation and on the basis of interaction between activated molecules. It is questionable, however, whether processes of this nature will be commercially able to compete with other known methods for the formation of methanol and formaldehyde.

Reactions in the Presence of Oxides of Nitrogen

It has already been seen that formaldehyde may be produced by the direct oxidation of methane at atmospheric pressure and that the formation

of methanol by this method has not been realized. While this may be accounted for on the basis that the alcohol is so much more readily oxidized than the hydrocarbon that only insignificant concentrations are permitted to build up, or that any alcohol formed is immediately decomposed, it is probable that methanol, as such, may never form since the oxygen by reacting in molecular form carries the methane directly to formaldehyde by the splitting out of water from the unstable dihydroxymethylene intermediate. Normally the reactivity of the formaldehyde thus formed permits its ready oxidation to the ultimate products, water and carbon oxides, or its decomposition to hydrogen and carbon monoxide, but by proper control some formaldehyde may be produced.

If the oxidation of methane could be conducted under such conditions that only atomic oxygen is reactive and that the oxygen supply is so limited that only controlled secondary oxidation of intermediately formed compounds could occur, it is possible that not only larger yields of formaldehyde would be obtained but also that yields of methanol would be possible. The attainment of these conditions has been the object of some work with nitrogen oxides as catalysts and as oxidants. The results have been of sufficient interest and importance to warrant several publications and patents.

The superiority of the nitrogen oxide catalysts over the solid catalysts may also in part be due to the homogeneous type of reactions possible in such gas mixtures as have been used. It is quite probable that the formaldehyde is adsorbed more strongly on the solid catalysts than is methane with the result that it is subjected to even more severe oxidation conditions than would be the case in the absence of active solid surfaces.

The large amount of work that has been done with solid catalysts has shown that most of the materials tried had little or no directional catalytic activity in the oxidation process. It was noted, however, that whereas alumina prepared by heating the hydroxide was inactive as a catalyst, that obtained by heating the nitrate was the most effective of the solid catalysts. This led to the discovery that nitrogen oxides were the effective catalysts, and prompted the development of this type of catalyst.[117]

Bailey [118] has claimed the use of a mixture of one volume of methane, two volumes of nitric oxide with sufficient oxygen or air to unite with the nitric oxide and convert it to nitrogen peroxide. This mixture is passed through a tube of porcelain or other material not affected by the gases at a temperature of about 450° C. The formation of nitric or nitrous acid would be destructive to the object of the process by oxidizing the formaldehyde further to water and carbon dioxides, and is prevented by the use of lime to absorb the water formed during oxidation and by passing the reaction products through a slurry of calcium carbonate to neutralize the mixture. Purification of the product resulting from this

[117] Bibb and Lucas, *Ind. Eng. Chem.* 21, 633 (1929).
[118] Bailey, U. S. Pat. 1,319,748 (1919).

process is troublesome due to the facts that nitric oxide is not removed in the alkaline slurry and that the formaldehyde obtained from the solution by distillation contains nitrogen oxides difficult to remove.

Experiments in which methane was oxidized directly by nitrogen peroxide, which splits off one atom of oxygen per molecule, failed to yield any methanol.[18] The lack of methanol in the products is probably due to decomposition at the temperatures used rather than to reoxidation to formaldehyde, since the gas mixtures were so made up that insufficient oxidant was present to carry the hydrocarbon to the aldehyde stage unless a certain portion of the molecules had been acted on preferentially, which is unlikely because of the homogeneous nature of the reaction.

Contrasted with these processes is that of Bibb [119] by which methane is oxidized by oxygen in the presence of small amounts of nitric acid fumes which act as catalysts in the reaction. The low concentration (not more than one to two per cent by weight of the methane-air mixture) of nitrogen oxides is obtained by bubbling the gas mixture through concentrated nitric acid maintained at 22° to 24° C. The mixed gases are preheated and passed into a reaction chamber filled with broken fire-clay and maintained at a temperature of 250° to 560° C. The methane is apparently oxidized to formaldehyde by way of methanol and in accordance to the hydroxylation theory of Bone.[9] Some formic acid is also formed. A ratio of formaldehyde to methanol of 5 to 1 is obtained by fractionally distilling the products of the oxidation.[120] Some of the published results obtained by the process disclosed in this patent may be misleading because a natural gas containing 7 per cent ethane had been used.[117]

Recently reported results * from the Bibb process furnish data from which the economic possibilities may be deduced. With a natural gas containing 80.40 per cent methane and 16.55 per cent ethane yields of 123.3 grams formaldehyde per thousand liters of gas were obtained in a four pass system. With the same gas but in a recycle system yields of 170.2 grams of formaldehyde per thousand liters of gas are reported. The ratio of nitrogen dioxide (from nitric acid) to formaldehyde by weight was, in the first case, 1 to 2.97 and, in the second case, 1 to 3.23. With a gas comprising 90 per cent propane yields of 127.9 grams formaldehyde per thousand liters were obtained in a single pass at a nitrogen dioxide to formaldehyde ratio of 1 to 4.83 by weight.

Although the runs with natural gas presented above were made with a reactor wall temperature of 735° C., the mols of formaldehyde produced do not exceed the mols of ethane introduced with the natural gas. Thus the yields of formaldehyde obtained were: 4.1 mols in the four pass and 5.67 mols in the recycle systems per thousand liters of gas, whereas 7.4 mols of ethane were introduced per thousand liters of natural gas (calcu-

[18] Frolich, Harrington and Waitt, *loc. cit.*
[119] U. S. Pats. 1,392,886 (1921) Reissue 15,789 (1924); 1,547,725 (1925); Can. Pat. 302,672 (1930) Bibb.
[120] Zimmerli, *Ind. Eng. Chem.* 19, 524 (1927).
* Bibb, Pet. Div., Am. Chem. Soc. meeting at Buffalo, N. Y., September 1, 2, 1931.

lated at standard conditions). Although this should not be taken as proof that the formaldehyde comes entirely from the ethane, it should be considered when comparisons are made with results obtained from "natural gas" of different composition by other processes. The excellent yields of formaldehyde obtained from propane by the Bibb process, considering that only single pass data are shown, lend weight to the belief that the higher molecular weight hydrocarbons present in hydrocarbon gas mixtures, composed mainly of methane, are the major source of the formaldehyde produced in oxidation processes.[122]

The gases leaving the scrubber and containing nitrogen oxide gases may be used again in the cycle of operations which thus becomes a continuous process. That the oxides of nitrogen act catalytically is shown by the fact that they are not reduced but come out of the reaction zone in the same amounts as they entered and also by the fact that if the amount of these oxides is increased much above the one to two per cent of the total gas mixture, as recommended, they become a serious detriment to the formation and recovery of the products. The claims are extended to the oxidation of higher members of the methane series of hydrocarbons, and to the use of other gaseous oxides or oxygen acids or oxides which will volatilize at the temperature of the reaction chamber, such as sulfur oxides, carbon oxides, etc. However, this latter claim does not appear to have any justification since it has been shown [121, 47] that sulfur dioxide and trioxide have no catalytic effect on the oxidation, and it is well known that carbon dioxide is not active as an oxygen carrier at the temperatures used in partial oxidation in the absence of active specific catalysts.

Concentrations of 1 to 2 per cent of nitrogen oxides have a very remarkable influence on the reaction between methane and oxygen, and yields of oxygenated products have been obtained that are much larger than those obtained otherwise. Thus, Layng and Soukup [47] were able to obtain 25 mg. methanol, 205 mg. formaldehyde, and 76 mg. of formic acid per liter (normal temperature and pressure) of methane decomposed, a yield of oxygenated products corresponding to a carbon efficiency of about 17.5 per cent. Nevertheless, Smith and Milner [122] found that a temperature of 500° C. was necessary before appreciable reaction occurred with nitrogen oxide catalysts, and that regardless of the total methane decomposition in the range 3 to 50 per cent, the volume of formaldehyde never exceeded the volume of nitrogen oxides used. The major products were water and carbon monoxide, and the highest conversion of methane to formaldehyde per pass was 3.7 per cent. Contrary to the opinion of Bibb and Lucas,[117] these workers found that almost none of the nitrogen oxides could be recovered after reaction with methane, a fact indicative of a reduction to nitrogen by methane or hydrogen.[123] The excessive cost of

[121] Berl and Fischer, *Z. angew Chem.* **36**, 297 (1923).
[122] a. Smith and Milner, *Ind. Eng. Chem.* **23**, 357 (1931); b. *Ind. Eng. Chem. News Ed.* **8**, No. 16, 19 (1930).
[123] Gibson and Hinshelwood, *Trans. Faraday Soc.* **24**, 559 (1928).

nitrogen oxides relative to the value of formaldehyde produced prevents the practical application of the process to formaldehyde production.

The mechanism is complex, but seems to involve the formation of a loose compound between methane and nitrogen oxide which decomposes, as the temperature rises, to yield formaldehyde. The formaldehyde partly decomposes to hydrogen and carbon monoxide and the nitrogen oxide reacts further until completely reduced to nitrogen. The hydrogen formed finally appears as water.

Reactions in the Presence of Chlorine

When a mixture of methane, oxygen, and chlorine is burned, a reaction represented by the overall equation

$$CH_4 + 2O_2 + 2Cl_2 = CO_2 + 4HCl + O_2$$

occurs.[124] The oxygen combines preferentially with the carbon, and the chlorine with the hydrogen. With insufficient oxygen, carbon monoxide is formed rather than the dioxide as written above.

By properly controlling the reaction, it is possible to stop the oxidation short of completion and form intermediate products such as formaldehyde in good yield,[125] according to the claims. The gaseous mixture of hydrocarbon (preferably methane), oxygen, or air, and chlorine is preheated to reaction temperature and then passed over a suitable catalyst at temperatures of from 400° to 500° C. By using a mixture consisting of 4 parts of methane, 1 part of oxygen, and 1 part of methyl chloride or its equivalent in methane and available chlorine, and contacting with powdered barium chloride at 480° C. for about 5 seconds, 8 to 10 per cent of the methyl chloride is converted to formaldehyde and a somewhat larger proportion oxidized to carbon oxides per passage. The use of hydrocarbons higher than methane in the process is objectionable from the standpoint of recovery since a mixture of compounds is obtained that is difficult to separate and purify.

A possible method for the production of methanol from methane is through chlorination to methyl chloride followed by hydrolysis to methanol. Because of the relative cheapness of the reactants, the chlorination of methane has been rather thoroughly studied. It has been shown that by the use of diluents for heat control, it is possible to control the chlorination to such a degree that preponderating proportions of any one of the chlorination products may be obtained [126] at will.

Methyl chloride is much more stable than the higher alkyl chlorides. That it is slowly hydrolyzed by heating with alkaline solutions at 140° C. (20 to 24 atmospheres pressure) has been shown by Szarvasy.[127] Whis-

[124] Schlegel, *Ann.* 226, 140-2 (1884).
[125] a. U. S. Pat. 1,697,105 (1929) Carman; b. U. S. Pat. 1,697,106 (1929) Carman and Chilton.
[126] a. Jones and Meighan, *Bur. Mines Tech. Paper* No. 255 (1921); b. Boswell and McLaughlin, *Can. J. Research* 1, 240-255 (1929); c. Egloff, Schaad and Lowry, *Chem. Rev.* 8, 1-75 (1931).
[127] Szarvasy, *J. Soc. Chem. Ind.* 35, 707 (1916).

ton [128] states that methyl chloride and steam do not react appreciably below 270° C. but that formation of methanol was almost quantitative when methyl chloride was passed over slaked lime at 300° C.

Further details in regard to this process have been published by McKee and Burke.[129] From a study of the thermodynamics of the process, they conclude that equilibrium between steam and methyl chloride to form methanol is such that at 350° C. no methanol will form. However, equilibrium between methyl chloride and calcium hydroxide to form methanol and calcium chloride is so favorable that over 98 per cent of the methyl chloride can be converted. Their experimental results demonstrate the validity of these conclusions remarkably well. Indeed as they point out the process offers no engineering difficulties while giving high yields. The cost figures are such, however, as to prevent competition with the cheap methanol being produced from water gas. They estimate that with chlorine at 2 cents a pound, the gross cost of methanol would be 70.8 cents per gallon, which could be reduced, however, if an outlet could be found for the by-product hydrochloric acid from the original chlorination.

By the use of antimony pentachloride or cupric chloride the reaction between methane and diluted chlorine can be so controlled that yields of about 97 per cent of methyl chloride may be obtained. The method of forming methanol from this compound by passing a mixture of it with steam over lime at 350° C. is claimed to be used commercially.[130]

Reactions in the Presence of Ammonia

To overcome the objectionable reoxidation of formaldehyde and decomposition at the temperature of the reaction zone in the oxidation of methane, it has been proposed to react the formaldehyde as fast as formed with some substance to give a compound more stable under the conditions of the reaction and thus to increase the yields obtainable. It is claimed [131] that a reaction between the newly formed formaldehyde and ammonia to form a more stable compound, hexamethylene-tetramine, is possible under certain conditions, so that the formaldehyde is saved from destruction and can be obtained in a technically satisfactory yield. The hexamethylene-tetramine is prepared by oxidizing methane with air in the presence of ammonia gas. A mixture consisting of six volumes of methane, twelve volumes of oxygen, and four volumes of ammonia gas is passed through a constricted metal tube which is heated at the constriction. The tube is made of such a metal as copper, silver, nickel, steel, iron, or alloys of iron with tin, zinc, aluminum, or silicon or of iron coated with one of these metals. Contact material to act as a catalyst when non-catalytic tubes are used in the form of wire or sheets of silver, copper, tin, or alloys may be introduced in the tube. At atmospheric pressure a tube temperature

[128] Whiston, *J. Chem. Soc.* 117, 190 (1920).
[129] McKee and Burke, *Ind. Eng. Chem.* 15, 682, 788 (1923).
[130] Graetz, *Rev. Pétrolifère*, May 10, 1930, p. 657.
[131] Brit. Pat. 156,136 (1922) Otto Traun.

of 300° to 500° C. may be used while if vacuum is used the tube temperature may be 500° to 700° C. Yields as high as 70 per cent are claimed, and the formaldehyde may be regenerated from the hexamethylene-tetramine.

The claims of this patent have not been satisfactorily substantiated by independent workers. Schönfelder,[73] and Wheeler and Blair [11] were unable to duplicate the results claimed. According to the latter, ammonia has some stabilizing action on formic acid but does not stabilize the formaldehyde produced in methane oxidation. Indeed in the oxidation of paraffin hydrocarbons by means of oxygen containing gas in the presence of inorganic catalysts, it is claimed [132] that the reaction is accelerated by the addition of organic nitrogeneous bases such as hexamethylene-tetramine.

Reactions with Oxides of Carbon

Carbon monoxide may be considered as an unsaturated organic compound of high reactivity since it so readily undergoes decomposition to carbon dioxide:

$$2CO = C + CO_2.$$
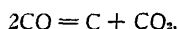
At 250° C. this reaction occurs with the liberation of almost 20,000 calories of energy per mol. In the presence of active catalysts especially, this decomposition of carbon monoxide to form carbon dioxide and a highly reactive carbon, complicates any attempt to use it as an oxygenating agent in vapor phase reactions.* Consequently, very little experimentation has been done with the direct object of reacting hydrocarbons with carbon monoxide to form oxygen containing compounds.

It is claimed [133] that methane may be oxidized to formaldehyde, methanol, and formic acid by heating with carbon dioxide for short periods of time over certain contact materials. The catalytic material may consist of copper, iron, nickel, cobalt, etc., and pressures of 12 to 50 atmospheres at temperatures up to 300° C. may be used. The reactor is usually constricted at the heated portion to obtain higher gas rates and consequent shorter times of contact than would be possible with larger tubes. Nickel carbonate or other carbonates having the power to dissociate at temperatures of 100° to 500° C. may be used and the product in this case is said to consist not of formaldehyde but of acetic acid.

Various electrical means have been proposed to effect reaction between difficultly reactive substances. For instance,[133c] a mixture of methane and an equal or greater volume of carbon dioxide is preheated and passed between the plates of a condenser in a high frequency circuit of high voltage to give formaldehyde. With a frequency of 1.5 million cycles and a voltage of 80,000 across the condenser plates, a yield of 150 to 210

[132] U. S. Pat. 1,762,688 (1930) I. G. Farbenindustrie.
* *See* Chapter IV.
[133] a. Brit. Pat. 156,148 (1922) Otto Traun; b. Brit. 226,248 (1923) Dreyfus. c. Brit. Pat. 353,076 (1930) (Ger., 1929) Gutehoffnungshutte Oberhausen.

grams of formaldehyde per cubic meter of methane is claimed at a linear gas velocity of 1.5 cm. per second. The possible use of a catalyst such as magnesium carbonate is also mentioned. These yields represent conversions of methane to formaldehyde of 11.2 to 15.7 per cent on a molal basis.

At temperatures of 700° to 800° C. methane begins to reduce carbon dioxide with liberation of carbon and at 950° to 1054° C. reacts readily to form carbon monoxide.[184] There is also evidence that higher hydrocarbons may react with carbon dioxide to form lower hydrocarbons together with carbon, hydrogen, and carbon monoxide.[185] The reverse of this reaction, the interaction of carbon monoxide with low molecular weight hydrocarbons to form higher hydrocarbons, resembles Fischer's process for forming hydrocarbons from mixtures of carbon monoxide and hydrogen, the hydrocarbons taking the place of hydrogen in the latter process. While this process is thermodynamically favorable at temperatures of 300° to 500° C. and pressures of 30 to 200 atmospheres, the necessity for using a highly specific catalyst to activate the hydrocarbon and the possibility of other side reactions occurring has prevented extensive experimentation. It must be realized that thermodynamic analysis of a process tells nothing in regard to the rate at which the reaction will occur, and is principally useful in indicating the possibilities of reaction.

The difficulty of causing methane to react with carbon monoxide at temperatures of 300° to 500° C. presumably would not hold in the case of ethane and propane which are known to crack into the corresponding olefines at temperatures slightly higher. However, methane is mentioned in a patent claiming the synthesis of hydrocarbons, etc., from mixtures containing carbon monoxide.[186a] This patent states that "it is quite easy to synthesize other hydrocarbons, especially liquid hydrocarbons or those readily liquefiable, in particular oxygenated compounds, in treating oxides of carbon with hydrogen or compounds rich in hydrogen, such as methane." Such catalysts as cerium, chromium, cobalt, manganese, molybdenum, osmium, palladium, titanium and zinc are mentioned. While the conditions are not clear it is possible that reaction of methane with carbon dioxide to form a mixture containing hydrogen and carbon monoxide might result in the formation of alcohols by the subsequent reaction of these products. Particularly high pressures of 800 atmospheres at 400° to 500° C. are claimed for the synthesis of methanol and other oxygenated products from mixtures of carbon monoxide and hydrogen in which the hydrogen has been largely replaced by methane.[186b]

It has also been claimed that organic oxygen-containing compounds may be prepared by the action of carbon monoxide on aliphatic or hydroaromatic compounds under pressure in the presence of such catalysts as

[184] Lang, *J. Gasbeleucht* 1, 932 (1888); *Gas*, 31, 932-40, 967-73 (1888); *Z. physik. Chem.* 2, 161-83 (1888).
[185] T. V. Moore, Graduate thesis 1929, Massachusetts Institute of Technology.
[186] a. French Pat. 468,427 (1914) Badische Anilin u. Soda Fabrik. b. Brit. Pat. 254,760 (1925) Badische Anilin u. Soda Fabrik.

aluminum chloride or bromide and zinc chloride.[187]   Examples of such contemplated reactions may be illustrated in the form of equations:

$$C_2H_6 + CO_2 = C_2H_5COOH$$
$$C_2H_6 + CO = C_2H_5CHO$$
$$C_6H_6 + CO_2 = C_6H_5COOH$$
$$C_6H_6 + CO = C_6H_5CHO.$$
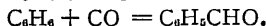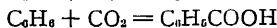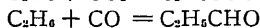
Thermodynamic analysis indicates that such reactions are on the whole unfavorable.   Furthermore, the complexity and uncertainty of the mechanism by which such reactions may occur makes the choice of proper catalysts largely an empirical selection.   However, it must not be overlooked that such reactions as the Kolbe-Schmitt synthesis of salicylic acid from dry sodium phenoxide and carbon dioxide represent processes, the success of which might point the direction to the solution of the problems attending the realization of the type reactions mentioned above.

Attempts have been made to use highly reactive compounds of carbon monoxide such as phosgene [188a] and metallic carbonyls [188b] in reactions with gaseous paraffin hydrocarbons to form aldehydes, ketones, or other organic compounds.   Such reactions constitute a very interesting field of work which has not been exploited largely because of major difficulties in the production and handling of the intermediates.

Reactions with Water to Form Oxygenated Hydrocarbons

One of the early attempts to synthesize methanol was by the interaction of methane and water (steam) as shown by the reaction:

$$CH_4 + H_2O = CH_3OH + H_2.$$
$$\textit{methane} \qquad \textit{methanol}$$
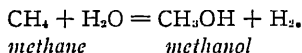
All attempts to realize the reaction failed,* and had the data been available for a thermodynamic analysis, no attempts would have been made since the equilibrium is very unfavorable.

$$K \text{ (400° C.)} = \frac{p_{CH_3OH} \times p_{H_2}}{p_{CH_4} \times p_{H_2O}}$$

is of the order of 4×10^{-6}, and may be in error 50 per cent in either direction without affecting the conclusiveness of the result.

It is possible also by dividing the reaction into steps to show the futility of attempting the synthesis.   Thus:

$$CH_4 + H_2O = CO + 3H_2 \qquad \text{(a)}$$
$$CO + 3H_2 = CH_3OH + H_2 \qquad \text{(b)}$$
$$\overline{CH_4 + H_2O = CH_3OH + H_2.} \qquad \text{(c)}$$
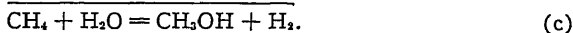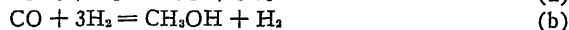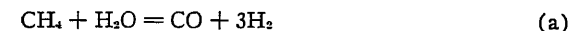
Reaction (a) has been discussed in Chapter IX and shown to require a temperature of 600° to 1000° C. for operation even in the presence of an

[187] French Pat. 671,241 (1928) I. G. Farbenind.
[188] a. French Pat. 680,586 (1928) Fohlen; b. French Pat. 680,585 (1928) Fohlen.
* *Compare* Dreyfus, Brit. Pat. 337,410 (1929).

active catalyst. Reaction (b) (Chapter IV) is favorable at room temperature but reverses at higher temperatures, so that methanol is completely decomposed at 350° C. and one atmosphere total pressure. Thus the overall reaction (c) is composed of two steps on which temperature has opposite effects. Furthermore, pressure is of no advantage since the reaction occurs with no change in volume.

In the case of the higher paraffin hydrocarbons the reaction with water to form alcohols may be visualized to occur in steps as follows:

$$C_3H_8 = C_3H_6 + H_2 \tag{d}$$
$$C_3H_6 + H_2O = C_3H_7OH \tag{e}$$
$$\overline{C_3H_8 + H_2O = C_3H_7OH + H_2} \tag{f}$$

or as:

$$C_3H_8 = C_2H_4 + CH_4 \tag{g}$$
$$C_2H_4 + H_2O = C_2H_5OH \tag{h}$$
$$\overline{C_3H_8 + H_2O = C_2H_5OH + CH_4.} \tag{i}$$
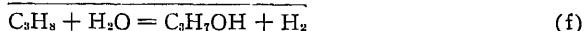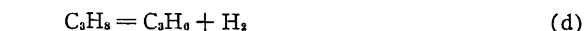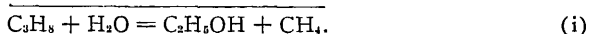
As in the case of methane, reaction (f) in which hydrogen is split off is extremely unfavorable from a thermodynamic standpoint. When a hydrocarbon is split off, however, as in reaction (i) the equilibrium is more favorable,

$$K_{(400° \text{ C.})} = \frac{p_{C_2H_5OH} \times p_{CH_4}}{p_{C_3H_8} \times p_{H_2O}}$$

being of the order of 0.04. Although no experimental evidence is available in regard to reactions of this nature, it may be concluded that the low yields obtainable and the difficulties involved will prevent any industrialization.

OXIDATION OF ETHANE

Mechanism

Since the formation of a greater number of products is possible in the oxidation of ethane, the mechanism is very much more complex than in the case of methane. Consequently the products obtained and their proportions vary widely in the results which have been published. In general the mechanism, aside from its greater complexity, may be considered as essentially the same as that involved in the oxidation of methane. However, as the hydrocarbon increases in molecular weight it becomes more and more easy to remove hydrogen from the carbon atoms with the result that as molecular weight increases the ease of oxidation increases likewise.

TABLE XII.—*Evolution of Heat on Addition of Oxygen Atoms to Hydrocarbon Molecules.*

Gas Phase Reaction	Heat Evolved [20] gm. cal./gm. mol	Heat Evolved per mol of O_2
$C_2H_6 + 1/2O_2 = C_2H_5OH$	28975	57950
$C_2H_5OH + 1/2O_2 = CH_3CHO + H_2O$	48450	96900
$CH_3CHO + 1/2O_2 = CH_3COOH$	66850	133700
$CH_3COOH + 2O_2 = 2CO_2 + 2H_2O$	192700	96350

That this is so has been shown experimentally.[130] When ethane mixed with insufficient oxygen for complete combustion was heated in borosilicate glass bulbs at temperatures of 250° to 400° C. under pressures of 1.75 to 2.33 atmospheres, carbon monoxide, carbon dioxide, oxygen, and unreacted hydrocarbon were among the end products. By circulating a mixture of ethane and oxygen under reduced pressure through a tube kept at 400° to 500° C., the gaseous products contained carbon monoxide, carbon dioxide, hydrogen, ethylene, oxygen and unreacted ethane. The water used for scrubbing the gases contained traces of formaldehyde and acetaldehyde. In the case of methane considerably higher temperatures have been found necessary for comparable reaction.

By exploding mixtures of ethane and oxygen in borosilicate bulbs, carbon monoxide, hydrogen, methane, acetylene, and ethylene have been obtained.[10, 140] As the initial pressure is decreased the amount of unsaturated hydrocarbons and water in the products showed a tendency to increase. The fact that no carbon is produced in these experiments and that water and ethylene are formed lends support to Bone's hydroxylation theory since it is probable that the alcohol formed in the initial step is dehydrated immediately to yield unsaturated hydrocarbon and water. The presence of hydrogen and aldehyde, especially at lower initial pressures, is also indicative of alcohol dissociation. The failure of any ethanol to appear in the product does not preclude its formation and immediate decomposition. It is hardly to be expected that ethanol if formed would exist long enough to pass out of the reaction zone and appear in the product since it is known that at the temperature of the oxidation process ethanol is entirely unstable.

Formaldehyde may be formed with greater ease from ethane than from methane and in better yields, presumably because of the lower temperatures or shorter times of contact possible when using ethane.[141] By passing a mixture containing ethane and air in the ratio of 1 : 2 by volume at a rate of 27 liters per hour through a quartz tube 0.5 inch in diameter heated for two feet to a temperature of 700° to 710° C. and recycling part of the reaction mixture, a yield of 8.5 pounds of formaldehyde and 1.4 pounds of acetaldehyde per thousand cubic feet of ethane were produced. The yield of formaldehyde corresponds to a conversion of 7.4 per cent of the ethane treated. During the reaction a portion of the ethane was dehydrogenated to ethylene also. In the light of this it is possible that many of the results which have been obtained in the oxidation of methane and reported on the basis of methane reacted are misleading since quite probably the methane used contained small amounts of ethane or even higher hydrocarbons which reacted to yield the aldehydes.

From a study of the rate of thermal combination of oxygen and ethane in a static system at temperatures between 400° and 500° C. and

[139] Bone and Stockings, *J. Chem. Soc.* 85, 693-727 (1904).
[140] Andrew, *J. Chem.* Soc. 105, 444-56 (1914).
[141] Brit. Pat. 238,938 (1925) Marks.

pressures between 100 and 760 mm. of mercury, Thompson and Hinshelwood [142] concluded that the oxidation is probably a chain reaction. The rate of the reaction is affected by total pressure approximately as in a reaction of the third order, the effect depending upon the partial pressure of the ethane much more than upon that of the oxygen. They suggest that the first step in the reaction is the formation of an unstable peroxide. If this peroxide reacts further with oxygen, the chain is stopped; but if it reacts with more ethane to form unstable hydroxylated molecules the chain is continued. An increase in the amount of surface exposed to the gases retards the reaction. The chains are not long as may be concluded from a consideration of the temperature coefficient of the reaction and the influence of inert gases on the rate.

Catalytic Oxidation of Ethane

As is the case with methane, experiments have been performed with ethane for the purpose of separation of gaseous mixtures in analytical procedures. Phillips [37] found that ethane was oxidized in a 3.1 per cent mixture with air at 450° C. over palladium asbestos. Mixtures of ethane and methane are difficult to separate by preferential combustion over platinum or palladium but hydrogen may be removed from such mixtures due to its lower reaction temperature. [39] The nature of the products obtained from the hydrocarbon oxidation in these experiments was not reported.

By using pumice, asbestos, or copper as catalysts, Glock [14] claims the formation of acetaldehyde, acetic acid, and ethanol from the oxidation of ethane. The fact that practically the same conditions of operation are used for ethane as were used for methane oxidation makes it seem rather doubtful that products having the same number of carbon atoms as the original ethane should have been obtained in view of the fact that methane is much more resistant to oxidation than ethane and requires more severe treatment.

The fact that ethane has been found to be so much more readily reacted upon by oxygen than methane to yield larger quantities of formaldehyde than is obtainable from methane, makes it seem that some of the high yields reported from methane may have in most part been due to ethane admixed in the hydrocarbon gas used, rather than the attainment of unusually productive operating conditions. This is true of data from experiments in which natural gas had been used for oxidation. The pressure oxidation process producing a mixture of methanol, formaldehyde, and acetaldehyde from natural gas utilizes the hydrocarbons higher than methane, and especially ethane.*

By mixing ethane and air in the ratio of one volume of ethane to two volumes of air and passing the mixture through a silica tube heated to

[142] a. Thompson and Hinshelwood, *Proc. Roy. Soc.* 125A, 277-91 (1929); *compare* b. Taylor and Riblett, *J. Phys. Chem.*, *Sept.* 1931. p. 2667.
* *Compare* page 177.

700° to 710° C. at such a rate that the time of contact is short, Curme [143] has been able to obtain good yields of ethylene, and aldehydes. In this process the period of heating is very short, being one second or less, and the spent gas is returned for further treatment. It is claimed that yields of 8.5 pounds of formaldehyde and 1.4 pounds of acetaldehyde are obtained per thousand cubic feet of ethane. In an example it is shown that 40.8 per cent of the ethane treated was converted to ethylene and aldehydes, 46.3 per cent remained unreacted, 11.7 per cent was converted to methane, carbon monoxide, and hydrogen, and 1.2 per cent was converted to carbon dioxide. It is possible to use propane, butane, or higher paraffins in a similar way to form higher olefins, higher oxygenated hydrocarbons, together with formaldehyde and ethylene.

Lind and Bardwell [74] found that in the initial stages of the reaction between ethane and oxygen under the action of alpha radiation from radon the rate of reaction was nearly double that between oxygen and methane under comparable conditions, but that the velocity of reaction decreased sharply when the reaction was about 70 per cent complete. As in the case of methane, the yield of oxidation products was 75 per cent of the maximum theoretically possible on the basis of number of ions present.

Reactions with Ozone

By oxidizing ethane with ozone at 100° C. it has been possible to form ethanol, [144] an accomplishment that has not been experimentally demonstrated in either catalytic or non-catalytic atmospheric pressure oxidation with molecular oxygen. This work is consequently of considerable theoretical importance even though from an industrial standpoint the use of ozone is not practical, at least not with methane. Ethane and air containing 2.33 per cent of ozone were mixed at the top of a wide vertical glass tube in such proportions that ethane was always present in large excess. The glass reaction tube was packed with glass beads and was heated by steam condensing at atmospheric pressure. Complete disappearance of ozone occurred during passage of the gas mixture through the reaction tube. Water used to scrub and cool the exit gas mixture was found to contain ethanol, acetaldehyde, and acetic acid as well as traces of formaldehyde. The gases not absorbed by the water were found to contain no acetylene, ethylene, or hydrogen which is indicative of a mild oxidation under such conditions that no secondary reactions took place.

In continuing this work Drugman [145] used air containing 10 per cent of ozone and found that although ethane was oxidized but slowly at 15° C., the reaction was more rapid than with methane. At 100° C. with a large excess of ethane much less acetic acid was formed but more ethanol was recovered from the wash traps. In each instance acetaldehyde was the main reaction product. Drugman concluded from these results that

[143] U. S. Pat. 1,729,711 (1929) Curme assr. to Carbide and Carbon Chem. Co.
[144] Bone and Drugman, *Proc. Chem. Soc.* 20, 127-8 (1904).
[145] Drugman, *J. Chem. Soc.* 89, 939-45 (1906).

ethanol was the primary product of the reaction and that acetaldehyde and acetic acid were secondary products, a conclusion apparently well justified from the results. It is to be noted, however, that the mechanism in the case of ozone oxidation is different from that in which oxygen is used, due to the fact that with ozone it is possible for single atoms of oxygen to react with the hydrocarbon to form alcohols by the dissociation of the ozone at the temperature of reaction. Also due to the greater reactivity of the nascent oxygen atoms it is possible to obtain appreciable reaction at temperatures sufficiently low to insure stability of the ethanol against further oxidation by oxygen to carbon oxides and water, and against dehydration to olefins or dehydrogenation to aldehydes. The use of large excesses of ethane so dilutes the ethanol first formed that secondary ozonization to form aldehyde or acid is markedly suppressed and the production of ethanol thus assured. The fact that greater yields of ethanol were found at 100° C. than at 15° C. may partly be explained on the basis of reaction velocity. At 100° C. the reaction between the ethane and the ozone is sufficiently rapid to consume most of the ozone before mixing would allow the freshly formed and widely separated ethanol molecules to meet and react with other ozone molecules or oxygen atoms. At the lower temperature, however, the reaction rate of ethane with ozone to form ethanol is sufficiently slower than the reaction rate of ethanol with ozone to form aldehyde and acid that considerable mixing may occur with consequent secondary oxidation of the newly formed ethanol to give the larger yields of acid found.

OXIDATION OF PROPANE, BUTANE, ISOBUTANE

Catalytic Oxidation

The literature contains very few references, with the exception of those already noted in the pressure oxidation of methane, to the oxidation of homologs of methane higher than ethane, such as propane, butane, and isobutane, indicative of a lack of interest in these hydrocarbons. This is probably due to the fact that much smaller quantities of the higher gaseous homologs are available at sufficiently low cost to warrant investigation, and to the extreme complexity of the resulting mixtures obtained.

Phillips [37] found that mixtures of air and hydrocarbon containing 3.1 per cent hydrocarbon were oxidized under the following conditions:

> propane over palladium-asbestos at 339° to 383° C.; isobutane over palladium-asbestos at 200° to 250° C.; isobutane over ruthenium-asbestos at 214° to 250° C.

Bone and Drugman [10] obtained aldehydes, methane, olefins, acetylene, carbon monoxide, water, hydrogen, and carbon by exploding mixtures of air and butane or propane.

The oxidation of butane and propane under the influence of radiation from radon did not go to completion as indicated by the appearance of liquid products other than water.[74] Prolonged exposure to the alpha radiation, however, gave complete oxidation in the case of propane.

Oxidation of all the saturated paraffin hydrocarbons up to isobutane in the presence of chlorine was found to result in the preferential reaction of the oxygen with the carbon to give carbon dioxide and of the chlorine with hydrogen to give hydrochloric acid gas.[124]

The reactions of mixtures of oxygen with propane and the butanes are classified into three types by Pease [140] on the basis of analyses made on the gaseous constituents from the reactions. At temperatures below the ignition temperature of mixtures of the saturated hydrocarbons and oxygen these types are: (1) Liberation of hydrogen by simple cracking to form the corresponding olefin; (2) removal of hydrogen by partial oxidation to yield an olefin, likewise of the same number of carbon atoms as the original hydrocarbon; and (3) removal from atoms of hydrogen as water and one atom of carbon as carbon monoxide, with formation of an aldehyde. The first two types appear to be normal gas reactions at 500° to 600° C., and are subject to induction by type (3) at lower temperatures. Type (3) may begin at 300° to 350° C. and is indicated as a chain reaction. Under suppression, no reaction may occur up to 500° to 600° C., then types (1) and (2) appear accompanied by type (3). Unfortunately the results and conclusions are not corroborated by analyses of the liquid products.*

Dehydrogenation

In the thermal decomposition of such saturated hydrocarbons as propane and butane or higher homologs for the formation of olefins, the cracking may occur over two routes, exemplified in the case of propane by dehydrogenation and demethanation as follows:

$$C_3H_8 \diagdown \begin{matrix} C_3H_6 + H_2 \\ \\ C_2H_4 + CH_4 \end{matrix}$$
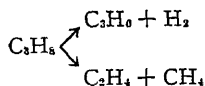
At the temperatures ordinarily used these two reactions occur with about equal velocities in the case of propane. Both of the olefins which are formed tend to polymerize and undergo further decomposition at this temperature (700° to 800° C.), the propylene at a much higher rate than the ethylene, with the result that either low yields are obtained or low conversions per pass through the cracking reactor must be accepted. A process which would enable a paraffin hydrocarbon to be converted to an olefin of the same number of carbon atoms by a dehydrogenation reaction would be highly desirable in some cases.

[140] Pease, *J. Am. Chem. Soc.* 51, 1839-56 (1929).
    * Burke, Fryling & Schumann, *Pet. Div., Am. Chem. Soc.* meeting, Buffalo, Sept. 1, 2, 1931, refer to new data which substantiate the chain reaction mechanism.

The free energy change for this dehydrogenation reaction

$$C_nH_{2n+2} = C_nH_{2n} + H_2$$
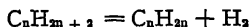
is represented by the following equation:

$$\Delta F = 44360 - 1550n - 41.7T \, [147].$$

For the reaction, as written, to occur ΔF must be negative, and the temperature required to make this so is sufficiently high to promote secondary reactions as pointed out above. However, because of the high free energy of formation of steam, the reaction between a paraffin hydrocarbon and oxygen to form an olefin and water is easily possible according to thermodynamic reasoning. Actually the partial removal of hydrogen by this means offers but small hope of success. The process is open to the same objections as the theory which postulates the intermediate formation of an alcohol in the oxygen or air oxidation of a hydrocarbon, namely, that oxygen is present and probably reacts as a molecule at the temperatures necessary to use. Also the greater reactivity of the olefins would leave them open to destruction by the same agency through which they would be formed, oxidation.

Nevertheless, it must not be overlooked that Henry [80] was able to remove hydrogen practically completely from mixtures with methane and ethylene without seriously affecting the hydrocarbons by oxidation in the presence of platinum and it is a common analytical practice to remove hydrogen from methane hydrocarbons by oxidation over copper oxide. That hydrogen atoms at the point of disrupting in the formation of an olefin from a paraffin should be capable of undergoing a similar treatment without effect to the olefin is not an impossibility. The use of oxides of metals capable of undergoing valence changes or capable of easy oxidation and reduction as oxidants for the process, together with careful temperature and time of contact control should meet with some success. By repeated oxidation and reduction it is possible to obtain a form of copper oxide which will oxidize hydrogen at temperatures as low as 100° C.,[148] and it is possible that long-lived catalysts sufficiently active at the temperatures desired can be produced.

Certain forms of active carbon have been found to promote the dehydrogenation of paraffin hydrocarbons in preference to demethanation. Steam activated brown coals treated at 800° to 900° C. are particularly effective. By passing oxygen into the reaction zone together with the hydrocarbon to be dehydrogenated the hydrogen formed may be removed as water.[149] Substantiation of the claims for this process are lacking, however.

At the present, processes concerned with the polymerization and dehydrogenation of paraffinic and olefinic hydrocarbons to form aromatics are also receiving considerable attention. The use of oxygen for the removal

[147] Francis. *Ind. Eng. Chem.* 20, 282 (1928).
[148] Taylor. *Trans. Am. Electrochem. Soc.* 36, 154 (1919).
[149] Can. Pat. 279,622 (1928) Herrmann and Baum assrs. to Consort. f. Elektrochem. Ind.

of the hydrogen and consequent promotion of the reaction has been claimed in a number of patents.[150]

Oxidation under Pressure

As has been shown already,* patents claiming the formation of alcohols, as well as aldehydes, acids, etc., from hydrocarbons of low molecular weight by oxidation under pressure have appeared recently. Oxidation, by this means, of hydrocarbons up to hexane has been claimed. An inspection of the critical data for the normal hydrocarbons from ethane to hexane shows that it might quite reasonably be expected that the reaction is vapor phase, except, perhaps, in the case of hexane. Liquid phase conditions are

Ethane	$T_c = 27°$ C.	$P_c = 48.5$ atms.
Propane	$T_c = 97°$ C.	$P_c = 44$ atms.
Butane	$T_c = 152°$ C.	$P_c = 37$ atms.
Pentane	$T_c = 197°$ C.	$P_c = 32.5$ atms.
Hexane	$T_c = 234°$ C.	$P_c = 28.8$ atms.

approached more nearly with the higher hydrocarbons, since as the molecular weight increases oxidation occurs at a lower temperature and the critical temperature becomes higher. Whether or not any significance can be attached to this from the point of view of reaction mechanism cannot be said because of a lack of data.

Advantage may be taken of this fact, that the higher hydrocarbons oxidize at lower temperatures, by using a lower pressure for the oxidation, since one of the functions of pressure is to lower reaction temperature to a point where decomposition reactions were slow, as has been postulated. Indeed with high molecular weight hydrocarbons (kerosene) it has been possible to recover oxidized products containing hydroxyl groups in the Tames atmospheric pressure process.† It should be noted, however, that Layng and Youker did not obtain heptyl alcohol from the atmospheric pressure oxidation of n-heptane.‡

In practically all of the claimed processes low concentrations of oxygen, based on the hydrocarbon, are mentioned as desirable. Methods proposed for obtaining these desired low concentrations and for preventing high oxygen ratios due to failure of equipment or control have been based on the solution of oxygen and nitrogen from high pressure air in the liquid hydrocarbons at room temperature.[105j] The meager data available for solubilities of oxygen and nitrogen in liquid hydrocarbons do not permit a determination of whether the air used for saturation will become richer or leaner in nitrogen or whether considerable amounts of nitrogen will

[150] a. U. S. Pat. 1,224,787 (1917) the use of iron oxide as a catalyst for the process; b. Brit. Pat. 265.234 (1926) I. G. Farbenind practices surface combustion at very high temperatures to form acetylene and polymerization products; c. Brit. Pat. 283,105 (1927). I. G. Farbenind use of chlorine in dehydrogenation at 300° C. over various catalysts.
  * Cf. page 178 *et seq.*
  † Cf. page 251 *et seq.*
  ‡ Cf. Ref. 4a, Chapter XI.
[105] j. U. S. Pat. 1,812,714 (June 30, 1931) Pugh, Tauch and Warren assrs. to Standard Oil Development Co.

have to be bled off from the reactors to prevent accumulation in undue amounts.* However, the indications are that oxygen is the more soluble and that excess nitrogen from the air may be vented at the saturators without the necessity for passing large quantities into the reactors with the hydrocarbon material.

The wide variety of catalysts that have been claimed for the pressure oxidation process throws some doubt on the real necessity for having a specific catalyst present in order to obtain the desired reaction rates. Indeed the claim for such a catalyst as borax coated copper makes it seem that the chief function of the "catalyst" is to distribute and help dissipate the heat generated by the reaction and prevent localized high temperatures which would jeopardize the continued existence of the desired intermediate oxidation products. By employing a divided metal of high heat conductivity, such as copper wire or turnings, and by coating it with some substance to prevent catalysis of decomposition reactions which are induced by some metals, the desired end would be attained. High gas velocities past these "catalysts," of course, mean short times of contact, but also may be important from the point of view of heat transfer from the gases to the solid heat conducting media. High surface velocities are conducive to a high rate of heat transfer, which is desired. By the use of low oxygen concentrations the extent of oxidation is limited and the possible temperature rise restricted. Nevertheless, thorough and rapid dissipation of the heat is required when large quantities of gases and vapors are to be passed through a limited reaction zone.

On the basis of the foregoing, general deductions relating to the operating conditions may be made as follows. The higher the pressure at which oxidation occurs, the higher will be the conversion to alcohols and the lower will be the conversion to aldehydes, acids, and water. A high rate of flow, i.e., high surface velocity over the "catalyst," is conducive to the formation of higher alcohols and a low rate of flow leads to the formation of larger proportions of water, lower alcohols, aldehydes, and acids. With other conditions fixed, an increase in temperature causes an increase in the secondary reactions with a consequent decrease in the conversion to higher alcohols. Also an increase in the concentration of oxygen lowers the efficiency at which oxygen is converted to useful oxygenated products, but tends to increase the yield of such products per pass through the reaction zone.

In general, the oxidized product from the pressure oxidation of hydrocarbons from ethane up to butane or higher in molecular weight may be expected to consist of a mixture of oxygenated organic compounds comprising alcohols, aldehydes, ketones, acids, esters, etc., together with water

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* The following data are available: Solubilities are expressed as volumes of gas at 25° C. and one atmosphere dissolved per volume of liquid per atmosphere. Oxygen in pentane—0.576 in the range 0–180 atms. Oxygen in gas oil—0.151 in the range 0–70 atms. Nitrogen in gas oil—0.100 in the range 0–80 atms. (Frolich, Tauch, Hogan, and Peer, Ind. and Eng. Chem. **23**, 548 (1931)). Air in mineral seal oil, 35° API—0.120 in the range 0–32 atms. (Dow and Calkins, *U. S. Bur. Mines Repts. Invest.*, No. 2732 (Feb. 1926).

and carbon oxides. The recovery and purification of the small amounts of desired products from the relatively large amounts of unreacted hydrocarbons and the water presents a formidable problem, especially with the higher hydrocarbons. No detailed accounts of the contemplated methods for separation of the product into useful constituents are available, but it is conceivable that the esterification of mixed alcohol fractions would furnish an outlet in the medium of a lacquer solvent. Another possible use for the alcohols would be in admixture with gasoline to furnish a non-knocking fuel, provided they could be produced at a low cost.

Results from the oxidation of propane with elemental oxygen at pressures of about 2000 pounds per square inch (136 atmospheres) and at temperatures of about 300° to 350° C. show that more than 40 per cent of the oxygen may appear in the form of liquid organic oxidation products.[105f] However, it must be remembered that oxygen concentrations of the order of only 5 to 15 mol per cent are used in the feed mixture and that, consequently, the per pass conversion of hydrocarbon to oxygenated product is not very high. A typical product from the oxidation of propane at 136 atmospheres pressure under such conditions consists of:

	Per Cent
Acetaldehyde and acetone	6.0
Methanol	22.0
Ethanol (95%)	37.0
Propanol (78%)	7.0
Formic acid	1.5
Water	26.5
	———
	100.0

OXIDATION OF PENTANE

Oxidation under Pressure

Yield data from the oxidation of pentane under pressure are available in a patent to the Standard Oil Development Co.[105k] Oxygen was dissolved in liquid pentane by passing air under pressure through a bubble tower down which the pentane was allowed to flow. The pentane thus treated contained approximately 5.5 mol per cent of dissolved oxygen, and was passed through a reactor under a pressure of 2200 pounds per sq. in. and at a temperature of about 278° C. The product was cooled and extracted with aqueous methanol. Analysis of the anhydrous, pentane-free product showed the following yield of oxygenated organic compounds:

Product	Grams per Liter of Pentane	Pounds per Gallon of Pentane (calc.)
Acetaldehyde	3.84	0.03205
Acetic acid	3.47	0.02895
Acetone	1.12	0.00935
Ethanol	4.52	0.03770
Propanols	4.00	0.03340
Butanols	1.20	0.01000

[105] k. Brit. Pat. 341,130 (1931) Standard Oil Development Co.

These data as presented in the patent are evidently conventionalized and the products designated probably represent characteristic fractions obtained in the distillation of the dry product. Substances not reported but which in all probability are present in the product include: methanol, formaldehyde, formic acid, esters, amyl alcohols, and possibly heavier compounds formed by condensation and polymerization.

Data on the efficiency of conversion of hydrocarbon to product or on the total per pass yields of product are not given. The propanols and butanols reported in the product are evidently mixtures of the isomers and no data are presented on the proportions of the isomeric alcohols present. Also no data are given as to the nature of the pentane, i.e., whether it was a mixture of isomers or a single pure isomer. Consequently, it is not possible to postulate on the mechanism by which the oxidation occurs. It is of interest to note, however, that under the conditions butanols are the highest molecular weight oxygenated compounds present in significant amounts. The presence of acetone in the product points to the presence of isopentane in the original hydrocarbon. Oxidation of isopentane would probably start on the longest "free" chain and meet a resistance point at the secondary carbon atom with the resultant formation of a ketone.

The total per-pass yields of anhydrous oxygenated organic product per gallon of pentane is about 0.151 pounds or about 0.0285 pounds per pound of entering pentane. This should be contrasted with the yields obtained in the case of the oxidation of aromatic hydrocarbons where complete oxidation of entering hydrocarbon to either product or water and carbon dioxide is aimed at. In the absence of data on the amount of destructive oxidation of the pentane no comparison of the heat evolution in the two cases is possible although it is safe to say that in the case of pentane the amount of heat evolved per unit of feed is much less than in the case of the aromatics because of the restricted amount of oxygen present in the former case.

Chapter VII

Oxidation and Hydration of Olefins and Acetylene

OLEFINS

Besides the sources of olefins mentioned in Chapter VI, all of the saturated hydrocarbons may be considered potential sources through "cracking" or dehydrogenation processes. This is particularly true of the gaseous paraffinic hydrocarbons since they are obtainable in comparatively simple mixtures at relatively low prices. Thus, propane, which is available in large quantities, is being marketed today as a compressed liquid with but a small admixture of other hydrocarbons. By means of a rather simple procedure it is possible to "crack" this propane to olefins with a carbon efficiency of about 80 per cent. The same is true of butane. Catalysts such as active charcoal,[1a] boron chloride or fluoride,[1b] oxides of zinc, magnesium, calcium, uranium, or silver,[1c] etc., may be used in the conversion of paraffins, especially those of two to eight carbon atoms, into the corresponding olefins with a minimum of demethanation, a reaction representing a loss of hydrocarbon material.[1d]

Gas from the cracking of petroleum oils is estimated to amount to the stupendous figure of 275 billion cubic feet for 1930.[2] This gas ranging in composition as shown in the table is unusually rich in olefin hydrocarbons. Gas from the vapor phase petroleum cracking processes, such as the Gyro process, is especially rich in olefins. In the Gyro process as much as 15 per cent by weight of the charging stock is obtained as gas, which may contain as much as 55 per cent olefins.

TABLE XIII.

Part I. Range of Composition of Gas from Cracking Processes.

	Per Cent
Ethylene	0.8 to 33
Propene	0.75 to 20
Butenes	0.25 to 10
Pentenes	0.2 to 1
Butadiene	0.5 to 1
Higher olefins	sometimes present
Hydrogen	2 to 7
Paraffins	40 to 90

[1] a. Brit. Pat. 301,402 (1927) I. G. Farbenindustrie; b. Ger. Pat. 489,960 (1930) Hofmann and Wulff; c. Brit. Pat. 330,623 (1929) I. G. Farbenind; d. Zanetti, *J. Ind. Eng. Chem.* 8, 674, 777 (1916).

[2] Egloff. Address before Production and Chemical Conference American Gas Assn., 1930, Cleveland, O.

Part II. Gas from Gyro Cracking Process.

(Total unsaturates, 54.9 per cent.)

Analysis of unsaturates

Ethylene	54.0
Propene	28.0
Butenes	9.0
Pentenes	1.7
Higher olefins	6.1
Butadiene	1.2

Oxidations of olefins in the vapor phase may for convenience be considered under two heads:

I. Oxidations taking place in the presence of gaseous oxygen in any of its molecular or atomic forms. Such reactions may or may not be simultaneously accompanied or almost immediately followed by secondary reactions of hydration, and yield as their principal products, aldehydes, ketones, acids and hydrogen.

II. Hydrations resulting in the primary addition of water and yielding alcohols as the principal products. When followed by secondary oxidation or dehydrogenation reactions the resulting product may contain aldehydes and acids.

Oxidation

Oxidation with Oxygen. There are but few references, in both the general and the patent literature, to processes which involve a study of the direct vapor phase catalytic oxidation of olefins. The major part of the experimental work has been concerned primarily with the development and substantiation of theories for the mechanism of the oxidation of both paraffinic and olefinic hydrocarbons. While a number of patents have been issued claiming the production of valuable oxygenated hydrocarbon products, it may be concluded that no process has been evolved for successful commercial exploitation. In general, the greater value of these olefins when used in processes more simple and more productive has deterred experimenters from projecting extensive research programs along this particular phase. In the few cases in which such a study has been undertaken the procedure has been to use either (a) molecular oxygen (air) or (b) ozone and to operate both with and without catalysts.

As early as 1879 Schutzenberger [3] discovered that when a mixture containing an excess of ethylene with oxygen was directed against a metal gauze heated at 400° C., noticeable quantities of aldehyde were produced. Later Bone and Wheeler [4] were able to show that combination between ethylene and oxygen could be effected at temperatures ranging between 250° and 500° C. even in the absence of catalysts. The experiments were conducted in borosilicate glass bulbs and also under reduced pressure in a "circulation" apparatus similar to that employed in earlier work on the

[3] *Bull. soc. chim.* **31**, 482 (1879).
[4] *J. Chem. Soc.* **85**, 1637 (1904).

oxidation of methane and of ethane.[5] In cases where closed glass bulbs were used the ethylene was mixed with one-half, double or four times its volume of oxygen and the action allowed to continue for different periods of time varying from hours to days. In all cases, the course of the oxidation was followed by exact gas analyses. The results showed that oxidation does not proceed with any rapidity below 500° C. and that the reaction apparently occurs in the homogeneous gas phase. Since formaldehyde is unstable at this temperature only traces of it were to be detected among the products of the reaction. The following mechanism was assumed to represent the progress of the oxidation:

$$C_2H_4 \xrightarrow{+O} \begin{array}{c} HCOH \\ \| \\ CH_2 \end{array} \xrightarrow{+O} \begin{array}{c} HCOH \\ \| \\ HCOH \end{array}$$

$$\begin{array}{c} HCOH \\ \| \\ HCOH \end{array} \longrightarrow 2H_2CO \longrightarrow 2CO + 2H_2$$

$$H_2CO \xrightarrow{+O} HCOOH \longrightarrow CO + H_2O$$

$$HCOOH \xrightarrow{+O} \begin{array}{c} OH \\ OH \end{array} > C = O \longrightarrow CO_2 + H_2O$$
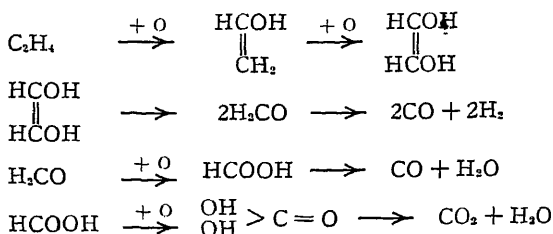
The following conclusions were drawn from the results of the work:

(1) When ethylene reacts with insufficient oxygen to burn it to carbon dioxide and water there is no evidence of a preferential combustion of hydrogen or carbon. The separation of hydrogen from the carbon atom is due entirely to thermal decomposition.

(2) Formaldehyde is the most prominent intermediate oxidation product and at low temperatures its formation is preceded by that of the less oxygenated products.

(3) Formation of aldehydes precedes that of water and carbon oxides.

(4) The secondary decomposition is determined by the temperatures. At temperatures above the ignition point formaldehyde decomposes into carbon monoxide and hydrogen giving the apparent result of preferential combustion of carbon, as when a mixture of equal volumes of oxygen and ethylene is exploded.

(5) The vinyl alcohol formed by the initial steps of the oxidation is rapidly further oxidized to unstable dihydroxyethylene and to formaldehyde, rather than rearranged to form the relatively stable acetaldehyde.

Because of the fact that formaldehyde is unstable at the temperatures required for the rapid oxidation of ethylene, it might seem reasonable to conclude that the reaction is not one which is capable of practical application. This conclusion would seem, at first sight, to be further supported by the fact that ethylene itself tends to decompose at temperatures in the neighborhood of 500° C. with the formation of methane, ethane, propene,

[5] *J. Chem. Soc.* **81**, 535 (1902); **83**, 1074 (1903); **85**, 693 (1904); *Proc. Chem. Soc.* **24**, 220 (1905).

butene, and higher olefins.[6] Ipatiew,[7] when employing a steel tube of 30 liters capacity, found that the polymerization of ethylene began at about 325° C., progressed fairly well at 350° C. and became quite rapid at 380° to 400° C. In other words, the oxidation of ethylene is further complicated by the fact that it is unstable at the more or less elevated temperatures which are required for its oxidation.

Further attempts for the adaptation of the oxidation process to the practical production of formaldehyde was due to the investigations of Willstätter and Bommer,[8] who studied the effect of different catalysts in accelerating the reaction. They were able to show in the first place that the initial temperature at which the oxidation begins varies greatly with the character of the catalyst.[9] For example, in the case of osmium this temperature was found to be as low as 130° C. In the second place, they were able to effect conversions of ethylene into formaldehyde in yields approximating 50 per cent of theory by applying the known fact that the stability of ethylene and the stability of formaldehyde both increase greatly with dilution.[10] Thus, by using ethylene mixed with a large excess of oxygen under reduced pressure, or ethylene mixed with oxygen and suitable quantities of an indifferent gas to act as a diluent, they were able to operate at even such relatively high temperatures as 530° to 580° C. and to obtain formaldehyde in concentrations such that it remained undecomposed. That the process has been patented [11] does not necessarily imply its practical nature. An example in this patent describes the oxidation of a mixture consisting of 20 per cent ethylene and 8 per cent oxygen with 72 per cent nitrogen. By circulating this mixture periodically through a catalyst chamber kept at 550° C. and periodically cooling it to remove the product, the process may be used for the continuous formation of formaldehyde.*

Very little special investigation appears to have been undertaken with a view to determining the effect of different catalysts in these reactions. Early work in the presence of palladium catalysts showed that mixtures of olefins with air were more readily oxidized than the acetylenes, while

[6] *Compare* Marchand, *Erdm. J. prakt. Chem.* 36, 478 (1845); Buff and Hofmann, *Ann.* 113, 129 (1860); Bone and Coward, *Proc. Roy. Soc.* 24, 222 (1905); Pring and Fairlie, *J. Chem. Soc.* 97, 498 (1910); 101, 91 (1912); *Proc. Roy. Soc.* 27, 305 (1911); Williams-Gardner, *Fuel* 4, 430 (1925); Frey and Smith, *Ind. Eng. Chem.* 20, 948-51 (1928); Walker, *J. Phys. Chem.* 31, 961-6 (1927).
[7] *Ber.* 44, 666 (1911).
[8] *Ann.* 422, 36-46 (1920).
[9] *Compare* Blair and Wheeler, *J. Soc. Chem. Ind.* 41T, 303 (1922); 42T, 87, 206, 343, 415 (1923).
[10] Undiluted ethylene is unstable above 350° C. and formaldehyde above 310° C. Investigations in regard to the physical constants and thermal decompositions of ethylene have been made by Berthelot, *Ann. chim. phys.* (3) 67, 53 (1863); (4) 9, 413, 455 (1866); (4) 12, 5, 22 (1867); (4) 16, 143, 148, 153, 162 (1869); Bone and Coward, *J. Chem. Soc.* 93, 1197 (1908); Thorpe and Young, *Proc. Roy. Soc.* 21, 184 (1873); Armstrong and Miller, *J. Chem. Soc.* 49, 74 (1886); Lewes, *Proc. Roy. Soc.* 55, 90 (1894) and 57, 394 (1895); Haber, *Ber.* 29, 2691 (1896); Pring and Fairlie, *J. Chem. Soc.* 99, 1796 (1911); Pring and Hutton, *J. Chem. Soc.* 89, 1591 (1906). For the polymerization of ethylene and olefine hydrocarbons in general *see* Zanetti, *J. Am. Chem. Soc.* 44, 2036 (1922); Ipatiew, *Ber.* 44, 2978 (1911) and 46, 1748 (1913); Lebedeff, *J. Russ. Phys. Chem. Soc.* 42, 949 (1910); 43, 820, 1116; 43, 1124 (1911); Mereshkevski, *J. Russ. Phys. Chem. Soc.* 45, 1249, 1634 (1913); Castello, *J. phys. chem.* 28, 1036-48 (1924); also, *see* Ref. (6).
[11] Ger. Pat. 350,922 (1918) Willstätter.
* This is, however, always contaminated by the presence of traces of acetaldehyde.

the paraffin hydrocarbons were the most resistant. In any given homologous series the lower members appear to be the most stable toward oxidizing agents. The temperature at which initial oxidation takes place varies greatly with the nature of the catalyst, the activity of some of the metals studied being in the order of osmium, palladium, platinum, ruthenium, iridium, rhodium, and gold.[12]

Another patent [13] covering ethylene oxidation describes the reaction of a mixture of 85 per cent ethylene and 15 per cent oxygen by passage over a number of different catalysts at temperatures of about 500° C. Catalysts consisting of the oxides of boron or phosphorus or of salts of the acids in bulk or distributed on an inert carrier are claimed to give large yields of formaldehyde at 375° C. The oxidation in this case may also be carried out in a circulating system, the ethylene and oxygen being added periodically in amounts necessary to maintain the proper concentration, and the formaldehyde being removed periodically by absorption in water.

The formation of butadiene or its homologs by heating olefins or mixtures containing olefins with oxygen or gases containing oxygen in the presence of dehydrogenating materials such as iron oxide, iron chloride, sulfur, sulfur containing compounds, etc., has been claimed.[14] Diluent gases or vapors may be used and the process operated at normal, reduced, or increased pressure. The ease with which complete combustion occurs under conditions necessary for reaction, and the high degree of reactivity of the diolefins, as butadiene, make such a process of dehydrogenation of questionable utility. The yields obtained in practice would probably be low.

With an apparatus similar to that of Willstätter and Bommer [8] in which mixtures of ethylene and oxygen were passed once at a temperature of 405° to 540° C. through a heated tube containing a platinum or ferric oxide catalyst, Blair and Wheeler [15] found that no formaldehyde was formed even when the rate of gas passage was very rapid. This result is not surprising since it has recently been shown [16] that by oxidizing ethylene at a temperature as low as 100° C. in the presence of silica gels metallized with silver, copper, platinum, or palladium, no partial oxidation products are formed, and the reaction goes to form carbon dioxide and water. Operation without catalysts in the same apparatus and use of a shorter heating period at higher temperatures increased the yields although the total conversion decreased. The use of steam in the reaction mixture tended to stabilize the formaldehyde and prevent its immediate oxidation. Ammonia has an even stronger stabilizing effect. In a somewhat different apparatus which permitted recirculation, yields as high as 70 per cent were obtained by recirculating for as long as 24 hours. A reaction mechanism similar to that which had been used by Bone and Wheeler * in 1904 was

[12] Phillips, *Am. Chem. J.* 16, 163-87; 255-77; *Z. anorg. Chem.* 6, 213-59 (1894).
[13] Brit. Pat. 199,886 (1922) Badische Anilin u. Soda Fabrik.
[14] Brit. Pat. 15,049 (1913) Perkins.
[15] *J. Soc. Chem. Ind.* 41, 303-10T (1922).
[16] Reyerson and Swearingen, *J. Am. Chem. Soc.* 50, 2872 (1928).
* *See* page 206.

proposed for the oxidation. Oxidation of the formaldehyde decomposition products was assumed to be according to:

$$H_2CO \longrightarrow (H_2 + CO) \xrightarrow{+O} H_2O + CO \xrightarrow{+O} H_2O + CO_2.$$
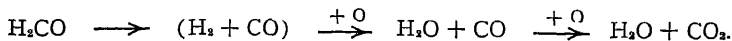
The possibility of vinyl alcohol rearrangement to acetaldehyde was recognized but not stressed. This rearrangement would make possible the oxidation of acetaldehyde to glycollic acid followed by decomposition and further oxidation of the decomposition products to water and carbon dioxide.

Using the methods developed in a study of the oxidation of methane,[*] Blair and Wheeler [17] further investigated the oxidation of ethylene. At 520° C. a 38.9 per cent yield of formaldehyde was obtained, together with large amounts of carbon dioxide and a little formic acid. At 560° C. with a large excess of oxygen over 50 per cent of ethylene went to acetaldehyde and 29 per cent to formaldehyde. At lower temperatures and with slow oxidation the rate of oxidation of acetaldehyde is less than that of formaldehyde. As the concentration or temperature of the gas mixture is increased, thermal decomposition of the ethylene begins to occur. Yields, however, at these conversions were necessarily low.

While the slow non-catalytic oxidation of ethylene apparently proceeds as a homogeneous gas phase reaction, the oxidation is affected by a variety of catalysts. Calvert [18] early showed that oxygen adsorbed by charcoal completely oxidized ethylene to carbon dioxide and water. The results of this work are of particular interest from the standpoint of the mechanism of the catalytic reaction. Oxygen adsorbed on charcoal is only removed with difficulty and when heat and vacuum are applied for this purpose, the oxygen is removed in the form of carbon oxides, showing that the "affinity" of the oxygen for the carbon atoms is stronger than the cohesive attraction between the atoms of the carbon. Apparently, however, collision of ethylene molecules with the adsorbed oxygen results in a reaction which loosens the bond between the carbon and the oxygen. Some idea of the nature of the C_xO_y complexes formed when oxygen is adsorbed on charcoal may be obtained from the heats of adsorption,[19] although it is questionable whether the real nature of this adsorbed oxygen is as yet known.

A similar mechanism has been postulated for the reaction when conducted in the presence of silica gel metallized with silver, gold, platinum, and palladium.[20] Collisions of ethylene molecules with oxygen molecules adsorbed and activated by the effective catalyst centers result in reaction. Collisions of oxygen molecules with adsorbed ethylene molecules, however, are ineffective.

[*] Cf. Chapter VI.
[17] J. Soc. Chem. Ind. 42, 415-7T (1923).
[18] J. Chem. Soc. 20, 293 (1867).
[19] a. Garner and McKie, J. Chem. Soc. 1927, 2451-7; b. Ward and Rideal, ibid. 1927, 3117-28; c. Wieland, Ber. 45, 2606-15 (1912).
[20] Reyerson and Swearingen, J. Am. Chem. Soc. 50, 2872-8 (1928).

The reactivity of the ethylene linkage is dependent to a large extent upon the substituents present in the molecule. The general effect for hydrocarbons is shown by the relative rates of combustion with oxygen of non-explosive mixtures.

Olefin	Ratio of Relative Rates [21]
Ethylene	1.0
Propene	1.7
Isobutene	2.8

Liquid phase oxidation with potassium permanganate shows a similar trend in the reactivity. The importance of the groups attached to the unsaturated carbon atoms is further shown by experiments on the action of potassium permanganate on more complex olefins.[22] The results have shown pentene, cyclohexene, and trimethylethylene are fairly easily oxidized but that diisobutylene and diamylene are surprisingly stable.

Recent investigations on the mechanism of hydrocarbon oxidation particularly as conducted from the standpoint of preventing automotive engine knocking have thrown considerable doubt on the hydroxylation theory of olefin oxidation. The rate of oxidation at higher temperatures and in the presence of catalysts is so high that it is practically impossible to isolate the intermediate steps for the purpose of formulating the mechanism of the process. As a result, no data are available at higher temperature from which conclusions may be drawn. However, it has been assumed that the slow oxidation at low temperatures indicates the mechanism at high temperatures sufficiently well to justify the use of such results in devising a mechanism.

Molecular oxygen combines with double bonds, at ordinary or moderate temperatures, to form peroxides.[23] These peroxides are, in general, but short lived and decompose into aldehydes or ketones or both, depending on the structure of the molecule:

$$\frac{R}{R'}{>}C=CH_2 + O_2 \longrightarrow \frac{R}{R'}{>}\underset{\underset{O-O}{|\quad|}}{C-CH_2} \longrightarrow \frac{R}{R'}{>}C=O + H_2C=O.$$
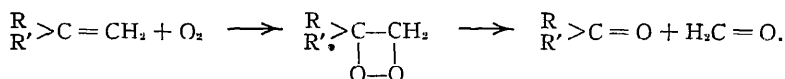
The interpretation of this general reaction for the cases of the simpler olefins gives reactions as follows:

$$CH_3CH=CH_2 + O_2 \longrightarrow \underset{\underset{O-O}{|\quad|}}{CH_3-CH-CH_2} \longrightarrow CH_3CHO + H_2CO$$

$$\frac{CH_3}{CH_3}{>}C=CH_2 + O_2 \longrightarrow \frac{CH_3}{CH_3}{>}\underset{\underset{O-O}{|\quad|}}{C-CH_2} \longrightarrow (CH_3)_2C=O + H_2CO$$

$$CH_3CH=CHCH_3 + O_2 \longrightarrow \underset{\underset{O-O}{|\quad|}}{CH_3CH-CHCH_3} \longrightarrow 2CH_3CHO.$$
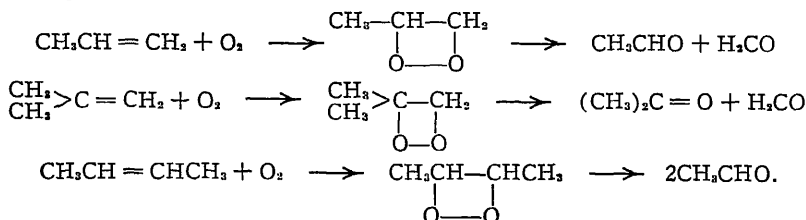
[21] Davis, *Ind. Eng. Chem.* 20, 1055-7 (1928).
[22] Howes and Nash, *J. Soc. Chem. Ind.* 49, 113T (1930).
[23] This has been shown in the case of amylene and hexylene by (a) Engler and Weissberg [*Ber.* 33, 1094 (1900)], and in the case of cracked gasolines by (b) Brooks [*Ind. Eng. Chem.* 18, 1200 (1926)].

While this mechanism seems much more plausible than that involving the splitting of the oxygen molecule with subsequent reaction to form vinyl alcohol from ethylene as proposed by Blair and Wheeler,[17] it does not explain the presence of the considerable quantities of acetaldehyde found by these workers in their product. The peroxide formed with ethylene might conceivably split to form formaldehyde but not to acetaldehyde. It is possible that the peroxide might react with another molecule of ethylene to give unstable hydroxylated molecules, such as vinyl alcohol, which might then rearrange to acetaldehyde in accord with the general scheme of the hydroxylation theory.[24] It is well known too that the olefins polymerize readily in the neighborhood of the temperatures used in the oxidation work and acetaldehyde may result from the reaction of oxygen with the higher olefins thus formed in accordance with the peroxide theory.

Further evidence in support of the peroxide theory has resulted from a study of the slow oxidation of pentene.[25] This work is of more particular interest from the point of view of paraffin hydrocarbon oxidation as applied to knocking phenomena, however, and will not be discussed here.

Recently, a chain type of reaction has been postulated for the oxidation of ethylene.[26] In highly exothermic vapor phase reactions such as the homogeneous oxidation of olefinic hydrocarbons conditions are particularly favorable for chain type reactions. The initial reaction in such transformations results in the formation of a molecule with excess energy and capable of readily reacting further with another molecule of the hydrocarbon to continue the cycle. Secondary processes such as absorption of the excess energy by a wall or surface, or destruction of the molecule by further oxidation serve to break the chain of reactions. The relative rates of formation and destruction of the active centers determine the speed of the reaction. Obviously, if the number of chains started is more than the number broken, the reaction becomes very rapid and explosion results. If the two rates are very nearly equal, the reaction proceeds with a measurable rate, the speed of which depends upon chain length. In general, the concentration of the reactants in the mixture determines the rates of formation and destruction of the chains and, hence, determines the rate of the reaction.[27] The first step in the chain would be the formation of an unstable peroxide which could then react with another molecule of ethylene to form an unstable hydroxylated molecule to continue the chain reaction. Further oxidation of the peroxide first formed, however, would end the chain. Supplementary data and additional evidence that this type of reaction occurs have been supplied by Spence and Taylor.[28]

The velocity of the reaction is measurable at 400° to 500° C. when the

[24] For an exposition of the theory regarding such molecular rearrangements *see* Henrich, "Theories of Organic Chemistry," translated by Johnson and Hahn, New York, John Wiley and Sons, Inc., 1922.
[25] Lewis, *J. Chem. Soc.* 1929, 759-67.
[26] Thompson and Hinshelwood, *Proc. Roy. Soc.* 125A, 277 (1929); Lenher, *J. Am. Chem. Soc.* 53, 3737, 3752 (1931).
[27] *See also* Bodenstein, *Chem. Rev.* 7, 215-23 (1930).
[28] *J. Am. Chem. Soc.* 52, 2399-2401 (1930).

mixture consists of ethylene and oxygen in the ratios $1:1$ or $1:2$. The net result of the reaction is according to the equation:

$$C_2H_4 + 2O_2 = 2CO + 2H_2O.$$
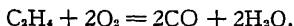
No trace of formaldehyde remains in the reaction products showing its almost instant decomposition at 400° C. Even at 200° C. there is evidence that further oxidation of formaldehyde occurs. The reaction rate is probably determined by the initial reaction of ethylene with one molecule of oxygen, the second molecule of oxygen being used up with much greater rapidity. As in the case of the oxidation of hydrogen, increased surface causes a real retardation in reaction rate and supports the contention that the reaction is of the chain type.

Liquid phase oxidation, a much milder form of oxidation than the various vapor phase processes that have been tried, may result in the formation of glycols.[29] By oxidizing 11 liters of isobutylene with a neutral one per cent potassium permanganate solution, Wagner was able to obtain 22 grams of isobutylene glycol (b. 177° C.), 4 grams of oxyisobutyric acid, and about 1.5 grams of acetone. Even in the case of ethylene appreciable yields of glycols were obtained. Ordinarily, the glycols are easily oxidized, in common with other alcohols, to yield aldehydes and acids or ketones depending on whether they contain primary or secondary alcoholic groups, respectively.

Recently, Lenher * has shown that the slow, non-catalytic reaction of oxygen and ethylene in the temperature range of 410° to 600° C. leads to the formation of ethylene oxide and formaldehyde as the principal products. Hydrogen peroxide is also formed. The formation of a peroxide or addition complex is postulated as the first step which is followed by a stepwise sequence of consecutive reactions leading in the end to the formation of carbon oxides and water. Work with propylene has indicated the probability of similar reactions taking place with the other olefins. Hydrolysis of the ethylene oxide leads to the formation of ethylene glycol, and a way is thus opened for the conversion of ethylene to glycol by a process involving only oxidation and hydrolysis. The direct applicability of catalysts to such an oxidation reaction for the purpose of increasing rate of reaction or increasing conversion to ethylene oxide is highly questionable in the light of present knowledge regarding chain reactions. However, low temperature oxidations such as those employed by Wagner seem to offer interesting possibilities for the formation of glycols.

Inflammability Limits

The inflammability limits in air for the lower olefins have been determined to be as follows:[30]

[29] Wagner, *Ber.* 21, 1232 (1888); Zeidler, *Ann. Chem. Pharm.* 186, 251.
[*] Lenher, *J. Am. Chem. Soc.* 53, 3737, 3752 (1931). These important papers appeared too late to receive adequate treatment here and should be consulted by the reader.
[30] Georgeson and Hartwell, *J. Chem. Soc.*, 1930, 733.

Olefin	Inflammability Limits Per Cent Hydrocarbon		Theoretical Mixtures Per Cent Hydrocarbon
	Lower Limit	Upper Limit	
Ethylene	3.30	18.25	6.51
Propene	2.58	7.50	4.44
Butene	1.93	6.00	3.36

The inflammability limits for ethylene-air mixtures have been found by White [31] to be:

Lower limit—3.25 per cent average ethylene.

Upper limit—34 per cent ethylene for upward propagation in a 7.5 cm. tube;
23.7 per cent ethylene for horizontal propagation in a 7.5 cm. tube;
15.5 per cent ethylene for downward propagation in a 7.5 cm. tube.

The limits, especially the upper limits, are slightly lower in smaller tubes due to the influence of the tube walls. The upper explosive limit of ethylene and air mixtures is raised from 16 per cent by volume of the hydrocarbon at 0 atmospheres pressure to 71 per cent at about 350 atmospheres pressure.[32] It is probable that in the experiments with ozone to be described that the ozone acted as a "trigger" to set off the reaction which occurs with explosive violence when the proper mixtures of oxygen and ethylene are present.[28]

Oxidation with Ozone

The application of ozone to the oxidation of ethylene was first investigated by Schönbein [33] in 1855 but neither he nor Otto who worked somewhat later,[34] succeeded in isolating the primary product of the reaction because of the heavy explosions which invariably took place.

In 1906 Harries [35] was finally able to obtain small quantities of formaldehyde as the result of a very painstaking investigation in which he used dry ozonized oxygen at temperatures of 15° to 18° C. The product, however, was not pure but consisted of a mixture of formaldehyde, formic acid, and hydrogen peroxide.

The first real knowledge of the mechanism of this reaction and also of methods for controlling it were arrived at a number of years later as the result of the very exact and extended investigations of Harries and his collaborators.[36] It was not until 1908, for example, that Harries and Haeffner were actually able to demonstrate that even the lower olefins will react with ozone without danger if greatly diluted with a low-boiling indifferent solvent. By using 7 per cent "ozone-oxygen" mixtures with

[31] For bibliography in regard to the limits of inflammability of ethylene-oxygen mixtures, *consult* White, *J. Chem. Soc.* 125, 2388 (1924).
[32] Berl, *Chimie et Industrie* 21, 452 (1929).
[33] Erdm. *J. prakt. Chem.* 66, 282 (1855); 105, 230 (1868).
[34] *Ann. chim. phys.* (7) 13, 77-144 (1898).
[35] *Ber.* 36, 2998, 3658 (1903); 37, 612, 839, 2708 (1904); 41, 3098 (1908); 42, 3305 (1910); *Ann.* 343, 311 (1905).
[36] a. "Ozonides of simple olefins," Harries and Haeffner, *Ber.* 41, 3098-3102; b. "Ethylene ozonide," Harries and Koetschau, *Ber.* 42, 3305-11 (1909); c. "Ozonides of phenols with unsaturated side chains," Harries and Adam, *Ber.* 49, 1029-34 (1916); d. "Ozonides of sym. butylene," Harries and Evers, *Ann.* 390, 235-68; e. Harries, *Ann.* 343, 311 (1905).

liquid ethylene and liquid methyl chloride from which all traces of moisture had been carefully excluded, the normal ozonide was isolated:

$$\underset{\diagdown\underset{O_3}{\diagup}}{CH_2 \text{---} CH_2.}$$
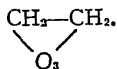
This substance is a colorless oil of the consistency of chloroform, very volatile and extremely explosive when rubbed with a glass rod, but, nevertheless, sufficiently stable to be distilled in a vacuum. It decomposes under the action of water in either one of the following ways:

(a) $C_2H_4O_3 = 2HCHO + O$ (nascent)
(b) $C_2H_4O_3 = HCHO + HCOOH$.

Neither decomposition is accompanied by the formation of any carbon monoxide or hydrogen.

Blair and Wheeler [37] passed mixtures of ethylene and oxygen containing 3 per cent ethylene through an Otto ozonizer and then washed the exit gases in water before collection. Determinations of formic acid, ozone, hydrogen peroxide, and formaldehyde were made. In some of the experiments coal gas was used as a source of dilute ethylene. In all cases, even with dilute gases, a rapid formation of formaldehyde took place through the formation and decomposition of ethylene ozonide:

$$C_2H_4 \xrightarrow{O_3} H_2C \underset{\diagdown\underset{O_3}{\diagup}}{\text{------}} CH_2 \xrightarrow{H_2O} 2CH_2O.$$
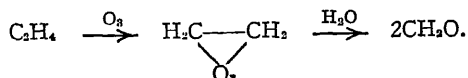
When the concentration of ozone was less than 1 cc. per liter of mixed gases, 90 per cent yields of formaldehyde based on the ozone were obtained. Use of higher concentrations of ozone lowered the yields. In the absence of water, the ozonide decomposes to formic acid and formaldehyde but with water present formaldehyde and hydrogen peroxide are formed. With dilute ozone very little secondary oxidation of formaldehyde occurs. The addition of ammonia to the gases raises the yield, probably because it protects the formaldehyde from further oxidation by the formation of hexamethylenetetramine.

Two patents, both of which describe the oxidation of ethylene by the action of ozonized oxygen, have been taken out in Germany and in the United States, respectively. According to the first [38] weakly ozonized oxygen or ozonized air mixed with ethylene and a spray of finely divided water particles is conducted over contact bodies at temperatures between 20° and 100° C., when a reaction takes place which results in the formation of a mixture of formaldehyde and glycol. Both substances may be obtained in excellent yields if the reaction products are immediately removed from further action by ozone or by the catalyst. This is effected

[37] *J. Soc. Chem. Ind.* 42, 343-6T; 347-50T (1923).
[38] Ger. Pat. 344,615 Plauson's Forschungsinstitut G.m.b.H.

by solution in the water vapor which is periodically smoked off. By varying the catalyst it is possible to increase the yield of glycol at the expense of the formaldehyde or vice versa. In this way, 50 to 60 per cent of glycol mixed with 15 to 30 per cent formaldehyde or 70 to 80 per cent formaldehyde mixed with 15 to 20 per cent glycol may be obtained. This conversion of the ethylene is practically complete but small quantities which may remain unacted upon may be mixed with water vapor or finely divided spray and again passed through the catalyst chamber. The latter consists of towers filled with porous material impregnated with the catalyst. If desired, the reaction may also be carried on in the absence of a catalyst.

The second patent [39] describes the conversion of ethylene into ethylene ozonide followed by the immediate decomposition of the latter into formaldehyde. The primary object in this process is to so regulate the reaction as to produce a large yield of formaldehyde or its polymerization product, paraformaldehyde, while reducing the formation of formic acid to a minimum. The procedure is similar to that which has been described in the case of the preceding patent and differs principally in the fact that no catalyst is employed. For example, ethylene, ozonized air and water vapor are introduced into a drum, tower, or other convenient form of apparatus which will facilitate an intimate mixture of the substances. The following reactions are supposed to occur:

$$C_2H_4 + O_3 = C_2H_4O_3$$
$$C_2H_4O_3 = CH_2O + HCOOH$$
$$C_2H_4O_3 + H_2O = 2CH_2O + H_2O_2.$$
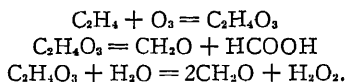
When steam at about the boiling point of water is used, the heat of reaction is sufficient to maintain this temperature within the drum and yields of 70 per cent formaldehyde along with 15 per cent formic acid are claimed. The use of superheated steam tends to increase the yield of aldehyde at the expense of the acid. The reaction products are first absorbed in water and then separated.

The work on ozonization of the ethylenic linkage has recently been extended to include some of the higher olefins.[40] The results of this work substantiate much of the earlier data and some of the patent claims as well. With ethylene the stable products were found to be formaldehyde and formic acid, and with propene, formaldehyde, acetaldehyde, formic acid, and acetic acid. By proper control of the conditions of the experiment it was possible to vary the ratios of the products obtained. Rather high efficiencies were obtained, corresponding to 90 per cent based on ozone and 75 per cent based on ethylene reacting under the most favorable conditions. However, when a gas obtained from petroleum cracking, containing 15 per cent of ethylene, 12 per cent of propene, and 8 per cent of butene was ozonized, the yields, while still high, were somewhat lower

[39] U. S. Pat. 1,423,753 Carter and Coxe, assrs. to S. Karpen Bros.
[40] a. Briner and Schnorf, *Helv. Chim. Acta.* 12, 154-81; 181-6 (1929); b. Briner and Meier, *ibid.* 12, 529-53 (1929).

than when ethylene alone had been used. With an excess of hydrocarbons present the yields were 79 per cent based on ozone and 59 per cent based on hydrocarbons, and with an excess of ozone the yields were 55 per cent and 68 per cent, respectively. Lower yields were also obtained with the three butenes and with a mixture of butenes obtained from cracking of a Mexican petroleum, the maximum yield in terms of ozone being 72 per cent in the case of 1, 2-butene.

The mechanism postulated in the light of this data is similar to that already shown and for the case of ethylene when water is present may be shown as:

$$C_2H_4 + O_3 + H_2O \longrightarrow CH_2(OH).O.O.CH_2(OH) \left\langle \begin{array}{l} 2CH_2O_2 + H_2 \\ CH_2O_2 + H_2CO + H_2O \end{array} \right.$$
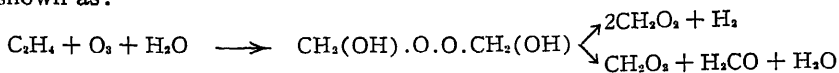
No results have been given of the effect of contact catalysis for these ozonization reactions but it would be interesting to compare the addition of ozone to an unsaturated bond with other similar addition reactions requiring the presence of polar walls, or catalytic surfaces.

HYDRATION *

The dehydration of alcohols to form the corresponding olefin is a well-known phenomenon. Thus, one of the standard laboratory methods for the preparation of ethylene is the dehydration of ethanol over kaolin at temperatures of about 500° C. and at atmospheric pressure. For this purpose the alcohol is heated in a suitable container in an oil bath or by other means to a temperature sufficient to cause the vapors to pass through the reaction tube at the desired rate. Lumps or sticks of kaolin or other catalyst are contained in an iron reaction tube externally heated to the desired temperature. Since the reaction is endothermic, large amounts of heat are required to maintain the temperature. The water resulting from the reaction is collected in a cooled trap and the gases then dried before condensing them in a steel cylinder which is cooled to a low temperature. The production of pure propene and butene may be accomplished in a similar manner by using isopropanol or secondary butanol in place of ethanol. In operation with the higher alcohol, however, the catalyst sometimes becomes covered with carbon deposited as a result of more violent decomposition of some of the products, such as cracking of the olefins, with the result that the activity is materially reduced. However, heating to red heat in the presence of oxygen is sufficient to revive it and the conversion returns to the value obtained with fresh kaolin when almost complete conversion is obtainable.

This process involving the dehydration of alcohols has been the subject of extended investigations. Since dehydrations of this type belong to the class of reversible reactions, an examination of this material is relevant.

* *Cf. also* Chapter II.

The very early work of Ipatiew, Sabatier, and Senderens [41] on the dehydration of the alcohols has already been referred to in Chapter II of this volume.

Sabatier [42] attributes the dehydration of alcohols over the surfaces of the oxides of thoria, alumina, and tungsten to the formation on the surface of these oxides, with the elimination of water, of a thin layer of an ester comparable to ethyl hydrogen sulfate. This ester is decomposed by heat into an olefin and the regenerated oxide. Thus:

$$ThO_2 + 2C_nH_{2n+1}OH = H_2O + ThO(OC_nH_{2n+1})_2$$
$$ThO(OC_nH_{2n+1})_2 = H_2O + ThO_2 + 2C_nH_{2n}.$$
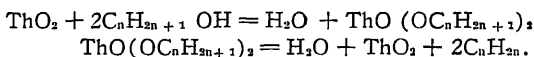
Although it has not been possible to isolate the intermediate ester formed in this way, it is possible to prepare the alcoholates of thorium and of aluminum by different methods, and to show that these compounds are decomposed at elevated temperatures into water, olefin, and the regenerated metallic oxide. However, the fact that titanium oxide which accelerates both the dehydration and dehydrogenation reactions can be made more selective toward dehydration by the addition of hydrogen to the alcohol vapors and more selective toward dehydrogenation by the addition of water vapor seems to point to a somewhat different mechanism for the catalytic action. This effect has been interpreted in favor of their hypothesis by the proponents of the adsorption theory.* The presence of added hydrogen, however, complicates the effect by introducing the factor of olefin hydrogenation which would result in the removal of olefin from the reaction in the form of saturated hydrocarbons.

By the use of different promoters it is also possible to alter the directional capacity of a given catalyst, by repressing selectively one or the other of the decomposition reactions. Thus by adding an agent more basic to the catalyst the dehydrating effect is repressed, and by adding an agent more acidic the dehydrogenating effect is repressed. In the production of acetone from isopropanol in the presence of zinc oxide, the quantity of propene formed is much reduced by the addition of small proportions of sodium carbonate to the catalyst. The addition of potassium carbonate to a uranium oxide catalyst increases and the addition of boric acid decreases the proportion of acetaldehyde to ethylene formed from ethanol. [43]

Although metals have generally been considered to exert only a dehydrogenating action in the reactions involved in the pyrolysis of the alcohols, it is possible for them to act toward dehydration in certain instances. By passing isopropanol over reduced copper at 320° C. it is possible to obtain acetone and propene, and by using ethanol, to obtain acetaldehyde and ethylene. By treating menthol in the same way menthene is formed. A determination of the water formed in each of these cases suggests that the catalytic action of the metal is one of direct dehydration. [44]

[41] Senderens, *Ann. chim. phys.* (8) **25**, 449-529 (1912).
[42] Sabatier and Mailhe, *Ann. chim. phys.* (8) **20**, 349 (1910).
* *Cf.* Chapter I.
[43] Brit. Pat. 323,713 (1928) E. I. duPont de Nemours & Co., Inc.
[44] Komatsu, *Chem. Abstracts* **18**, 1419 (1924).

A number of workers have studied a variety of catalysts for the dehydration reaction. For example, Whitaker and Backhaus [45] describe the preparation of ethylene by passing alcohol vapor, preheated at 300° to 350°, over alumina. Gilfillan [46] discusses the action of the oxides of silica, thorium, titanium and tungsten in inducing catalytic dehydrations and also gives a résumé of earlier work in this field. Bruss [47a] offers a study of the behavior of zinc oxide and anhydrous zinc sulfate as promoters; Hismaura,[47b] of the action of Adsol (a Japanese acid clay); Pease [47c] of the action of activated aluminas; Goris [47d] of the action of alumina and pumice; Brown [47e] of the action of the oxides of aluminum, thoria, silica and tungsten. Palmer [48] has made an extensive study of the behavior of metallic catalysts, especially those of copper. Bischoff [49] has investigated the action of different compounds of titanium. Adkins [50] and his co-workers have investigated the dehydrating action of zinc oxide and alumina with special attention to the effect of surface. The dehydration of propyl, isopropyl and amyl alcohols by passage over alumina has also been studied.[51]

The hydration of olefins to alcohols has been carried out on a large scale by hydrolyzing the sulfuric acid esters formed by the absorption of the olefins in sulfuric acid. In the case of the higher olefins these reactions occur with comparative ease. Thus, isobutylene may be hydrated to tertiary butanol in cold, moderately concentrated sulfuric acid.[52] Some of the pentenes and heptenes may be hydrated in dilute (5 to 10 per cent) solutions of formic, acetic, or oxalic acids as well as in weak solutions of the mineral acids.[53] With 60 per cent concentrations of hydroiodic acid, isobutylene yields the iodide almost exclusively, but at lower concentrations increasing amounts of the alcohol are formed.[54] Similar phenomena attend the absorption of the higher olefins in hydrobromic acid. Hydrochloric acid, on the other hand, does not show such marked activity toward the higher olefins and is practically devoid of activity toward ethylene.

That ethylene and water react only very slightly in the absence of catalyst, at elevated temperatures and pressures has been shown by Klever and Glaser,[55] who found that in 17 hours at 150° C. and 190 atmospheres pressure only 0.00011 mol of ethylene was hydrated per mol of water and at 200° C. and 100 atmospheres pressure, 0.0008 mol was hydrated. How-

[45] U. S. Pat. 1,421,640 (1922) Whitaker and Backhaus, assrs. to the U. S. Industrial Alcohol Co.
[46] *J. Am. Chem. Soc.* **44**, 1323 (1922).
[47] a. Bruss, *Bull. soc. chim.* **33**, 1433 (1923); b. Hisamura and Imacka, *J. Soc. Chem. Ind.* **43**, 233B (1924); c. Pease and Young, *J. Am. Chem. Soc.* **46**, 390 (1924); d. Goris, *Chimie et Industrie* **11**, 449 (1924); e. Brown and Reid, *J. Phys. Chem.* **28**, 1077 (1924).
[48] *Proc. Roy. Soc.* **106A**, 250 (1924).
[49] Bischoff and Adkins, *J. Am. Chem. Soc.* **47**, 807 (1925); *also compare* Adkins, *ibid.* **44**, 2175 (1922); **46**, 131 (1924).
[50] Lazier and Adkins, *J. Am. Chem. Soc.* **47**, 1719, 2291 (1925); Adkins and Perkins, *ibid.* **47**, 1163 (1925).
[51] Tranz and Winkler, *J. prakt. Chem.* (2) **104**, 44 (1922); Adams, Kamm and Marvel, *J. Am. Chem. Soc.* **40**, 1950 (1918).
[52] Butlerow, *Ann.* **144**, 22 (1867).
[53] a. Butlerow and Gorianow, *Ann.* **169**, 147 (1873); **180**, 245 (1875); b. Mikloschewsky, *Ber.* **24**, 269 (1891).
[54] Michael and Brunel, *Am. Chem. J.* **48**, 269 (1912).
[55] *Mitt. chem. tech. Inst. tech. Hochschule Karlsruhe* 1923, No. 1, 1-10.

ever, the addition of 1.93 per cent of hydrochloric acid resulted in the hydration of more than one mol of ethylene in a similar length of time. From this they concluded that ethyl chloride was first formed and then hydrolyzed to the alcohol and hydrochloric acid.* Ultra-violet light, sulfuric acid, and potassium acid sulfate have a polymerizing action on ethylene at elevated temperatures which hydrochloric acid does not, a point in favor of its use as a catalyst for the hydration. As hydrochloric acid is a strong dehydrating agent for ethanol, it should function as a strong hydrating catalyst for ethylene. However, hydrochloric acid requires elevated temperatures and pressures for reaction with both olefins and ethanol, whereas hydrobromic and hydroiodic acids react readily with either. Also, ethyl chloride is relatively quite stable.

In the case of hydrobromic and hydriodic acids and such olefins as isobutylene and trimethylethylene, the rate of alcohol formation may become such that it approaches the rate of hydrolysis of the corresponding alkyl halides, thus supporting the theory that halides are the necessary intermediate product.[54] The greater activity of the hydrobromic and hydriodic acids compared with hydrochloric acid toward ethylene is shown by the experiments of Swann, Snow and Keyes.[56] At 800 pounds per square inch pressure and a temperature of 150° C. no alkyl chlorides were detected when hydrochloric acid of from 5 to 25 per cent concentration was used. On the other hand, considerable yields of alkyl iodides were obtained under the same conditions when hydriodic acid was used, and alkyl bromides formed in the presence of 40 per cent concentration hydrobromic acid. Alcohol yields were very small. When using propene at 600 to 800 pounds per square inch pressure at 135° C. in the presence of 5 per cent hydrochloric acid solutions and solutions of silver nitrate, yields of alcohol several times that obtained from ethylene were found. The yields were still very low, however, even with times of reaction as long as one hour.

Wibaut and Diekmann [57a] found that by passing a stream of ethylene into a descending stream of sulfuric acid (65 per cent at 156° to 160° C.) a 5 per cent conversion to ethanol was effected. They conclude that the ethylene was absorbed in the acid to form ethyl sulfate which was subsequently hydrolyzed in solution to form ethanol.

In these liquid phase hydration processes the acid plays the rôle of a catalyst by forming esters with the olefins, which subsequently undergo hydrolysis to yield alcohols and release the acid. In the case of the higher olefins this intermediate esterification and hydrolization occurs as the olefins are passed into the solution, and free alcohols appear in the product. With the higher olefins practically complete hydration occurs even in dilute acids.[57b] However, in the case of the lower olefins, which dissolve

* *Cf.* Chapter VI.
[56] *Ind. Eng. Chem.* **22**, 1048 (1930).
[57] a. Wibaut and Diekmann, *Proc. Acad. Sci. Amsterdam* **26**, 321-8 (1923); b. Brooks and Humphrey, *J. Am. Chem. Soc.* **40**, 822 (1918).

only in the more concentrated mineral acids, hydrolysis of the esters cannot occur and it is possible to obtain only esters directly. It is necessary to dilute the resulting acid-ester solutions, in order to form the alcohols.

In support of the theory that the intermediate formation of alkyl esters occurs when dilute acids are used is the fact that olefins readily form addition compounds, because of their unsaturated nature, with certain substances and the claims that have been made for the hydrolysis of ethyl esters to ethanol. Almost 100 per cent yields of ethanol are claimed for the interaction of a mixture composed of 1 part of ethyl chloride and 10 parts of water by weight at 250° C. in the presence of catalysts composed of zinc, copper or cadmium sulfate or zinc chloride supported on active charcoal.[58] In such processes as this, high yields can only be obtained by recirculation of the unconverted alkyl halide, or by the use of abnormally long times of contact at the low temperature, with removal of hydrochloric acid.

A number of other processes have been proposed and patented for the hydration of olefins in the presence of aqueous solutions of various salts and acids under such conditions that liquid is present at temperatures of about 200° C. and above. However, commercial yields of alcohols have not been reported from these processes. Usually, fairly dilute solutions only of the stronger mineral acids have been used or proposed in order to avoid the polymerizing effects otherwise encountered.

By heating 2.0 grams of liquid ethylene with 10 cc. of a 4.3 per cent hydrochloric acid solution to 220° C. in a tube of 40 cc. volume, it is claimed that ethanol yields of 63 per cent of theoretical may be obtained. Other acids, such as sulfuric or phosphoric may be used in place of the hydrochloric. The operating pressure must be above 20 atmospheres,[59] and the temperature above the boiling point of water.

Ethylene is hydrated by heating at 150° to 250° C. with acidulated water under pressures of from 70 to 200 atmospheres. "Surface action" may be used to assist the reaction.[60]

Ethanol is produced from ethylene and liquid water under high pressure and at temperatures of 200° to 300° C. in the presence of dissolved or suspended salts such as silver nitrate, cuprous chloride, and mercuric chloride which have an affinity for ethylene. Bomb experiments only are described. For instance, by operating with 20 cc. of water in a 150 cc. bomb and 40 atmospheres of ethylene cold, and by heating to 300° C. for six hours without a catalyst only one per cent conversion of ethylene to ethanol is obtained. However, by using water saturated with mercuric chloride under otherwise the same conditions, a 10 per cent ethylene conversion is obtained.[61]

Secondary or tertiary alcohols are claimed to be produced by reacting

[58] Ger. Pat. 413,447 (1925) Badische Anilin u. Soda Fabrik; *Chem. Zentr.* 96, (II), 429 (1925).
[59] U. S. Pat. 1,607,459 (1926) Johannsen and Gross.
[60] Brit. Pat. 238,900 (1925); French Pat. 605,988 (1925) Röch. Eisen u. Stahlw. A.G.
[61] Brit. Pat. 308,468 (1928) Smith, Bridger and Imperial Chemical Industries Ltd.

the higher homologs of ethylene with a dilute acid or aqueous salt solution of acid reaction, in the presence of a catalyst composed of one or more compounds of bismuth or of a heavy metal of the first periodic group. Compounds of bismuth, copper, and silver are favored as catalysts. Partial pressures of olefins of about 10 atmospheres and temperatures of 100° to 250° C. are suitable.[62] It is claimed that ethylene is not affected under these conditions.

Thermodynamic consideration of the dehydration reactions indicates the possibility of synthesis of the alcohols from the olefins by reaction with water in the vapor phase under suitable conditions of pressure, temperature, and catalysis. Francis[63] has shown that in the temperature range 500° to 700° K (227° to 427° C.) the free energy of the dehydration of simple, aliphatic alcohols,

$$C_nH_{2n+1}OH = C_nH_{2n} + H_2O$$
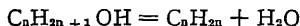
may be expressed as,

$$\Delta F = 15,110 - 1410\,n - 25.6T$$

where n is the number of carbon atoms in the alcohol and the corresponding olefin. From this value and the relation:

$$RT \ln K = -\Delta F,$$

the equilibrium constants for the dehydration reactions and for the reverse reaction may be obtained as shown in Table XIV.

TABLE XIV.—*Equilibrium Constants for Alcohol Dehydration.*

Reaction (gas phase)	$-\Delta F$ 450° C.	K 450° C.
$C_2H_5OH = C_2H_4 + H_2O$	$+6210$ cal.	76.2
$C_3H_7OH = C_3H_6 + H_2O$	$+7620$	202.0
$C_4H_9OH = C_4H_8 + H_2O$	$+9030$	543.0

Although the free energy equation as given was calculated for temperatures up to only 427° C., the error introduced by using it for calculations up to 450° C. is no greater than that inherent to the equation. Free energy calculations for reactions involving olefins are decidedly limited by the data available on the olefins themselves. There is considerable need for more data. Experimental determinations of the dehydration equilibria for alcohols would also be a valuable contribution. The values for the equilibria given here, while not accurate since they have been obtained by the use of a general equation, are sufficient to indicate the direction and magnitude of the effects, and to show the possibility for hydration of olefins.

The branched-chain primary alcohols are slightly more stable, just as the branched-chain hydrocarbons are more stable than the straight-chain hydrocarbons. Secondary and tertiary alcohols have still more negative free energies than the primary or normal alcohols. The free-energy equation shows that ethanol is stable to water and ethylene at temperatures

[62] Brit. Pat. 324,897 (1928); Can. Pat. 291,194; Fr. Pat. 662,968 (1928) I. G. Farbenind.
[63] *Ind. Eng. Chem.* **20**, 284 (1928).

below about 207° C. and hence, should be possible of synthesis by hydration of ethylene at temperatures below this at atmospheric pressure. The higher alcohols are more unstable and would require still lower temperatures for synthesis at low pressures. However, since the hydration reaction goes with a decrease in volume, it is possible to use pressure and thus obtain higher reaction rates by the use of higher temperatures, without the sacrifice of theoretical conversion.

It may be seen that the vapor phase hydration reaction occurs with a decrease in volume of 2 to 1,

$$C_2H_4 \quad + \quad H_2O \quad = \quad C_2H_5OH$$
$$\text{1 Volume} \qquad \text{1 Volume} \quad \text{1 Volume}$$
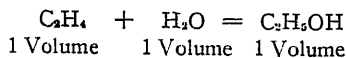
and may, hence, be markedly influenced by the application of pressure to go to the right. If it be assumed, for the purpose of exemplification, that $K = 80$ at 450° C. for the dehydration of ethanol to form ethylene and water, then for the reverse reaction,

$$K' = \frac{1}{80} = 0.0125 = \frac{[C_2H_5OH]}{[H_2O]\,[C_2H_4]}$$

where $[C_2H_5OH]$, $[H_2O]$, and $[C_2H_4]$ represent the concentrations of the components of the reaction mixture expressed as partial pressures in atmospheres. Concentrations are expressed as partial pressures and conversions calculated on that basis throughout since results sufficiently accurate to show the order of magnitude of the effect may thus be obtained. It should be noted that this value for equilibrium is very favorable to the hydration of ethylene under pressure even at a temperature of 450° C. More recent data indicate that it may actually be much less so. From the above expression it is evident that by increasing the pressure of either the steam, or ethylene, or both, the reaction will be made to go farther to completion.

It must be recognized, however, that by increasing the total pressure on the system by increasing the partial pressure of ethylene, other reactions are induced which are undesirable. Chief among these is the polymerization of the ethylene to form higher hydrocarbons, at this temperature chiefly olefinic in character. This polymerization reaction also occurs with a considerable decrease in volume and is markedly promoted by increase in pressure. Hence, to avoid these undesirable side reactions and still cause the reaction to occur in the desired direction, it is necessary to increase the partial pressure of the steam and maintain the partial pressure of the olefin at a relatively low value. By this means, good theoretical yields may be obtained if equilibrium be assumed. Thus, by operating at a temperature of 450° C. and about three atmospheres partial pressure of olefins and 200 atmospheres steam pressure about 70 per cent of the olefin would be converted to alcohol at equilibrium. If K for the dehydration of ethanol at 450° C. is as high as 120 (K' for the hydration of

ethylene is 0.00833), the conversion of ethylene at equilibrium will be decreased to about 60 per cent under the same conditions. Actually, these calculated conversions are probably too high since some recent calculations have shown that the original equation of Francis was too favorable for the hydration reaction.[64] The new equation of Francis shows:

$$\Delta F = -5320 + 815n + 17.2T - 0.5nT$$

for the dehydration of alcohols where n is, as before, the number of carbon atoms in the alcohol or corresponding olefin.

These latter calculations give a value of $K' = 0.00376$ for the hydration of ethylene or $K = 266$ for the dehydration of ethanol at 450° C. If this value represents more nearly the correct equilibrium, then the conversion of ethylene to ethanol under the above conditions would be decreased still further to a value of approximately 40 per cent. At atmospheric pressure and this temperature the decomposition of ethanol is practically complete at equilibrium.

The proper choice of catalysts for the vapor phase hydration of olefins under pressure to form alcohols is a very important factor. Apparently, catalysts active in promoting the hydration reaction are likewise active toward promotion of the undesirable polymerization reactions since this latter reaction often proceeds at a more rapid rate than that of alcohol formation as evidenced by the high yields of polymers and low yields of alcohols. The use of catalysts to lower the temperature for the reaction is necessitated by the fact that as the temperature is increased to obtain more favorable rates, the equilibrium conversion to alcohol becomes lower, and the tendency to polymerize is increased. Also, the catalyst must not promote dehydrogenation of the alcohol to form hydrogen and aldehyde since at the temperature of operation the equilibrium is very favorable for this reaction as has been pointed out in a previous chapter. Thus, the reaction, isobutanol = isobutyl aldehyde + hydrogen has an equilibrium constant corresponding to about 72 per cent decomposition at 450° C. even with 100 atmospheres of hydrogen pressure.

The experiments of Wibaut and Diekmann [57] were perhaps the earliest to indicate the reversibility of the dehydration of ethanol to ethylene and water vapor. These workers found that when a mixture of water vapor and ethylene was passed over aluminum oxide or sulfate at 300° to 400° C., the reaction product contained 0.2 to 0.4 per cent of acetaldehyde. This was not the result of oxidation of ethylene as was shown by passing ethylene and air over the same catalysts at 360° C. From this they concluded that hydrolysis to alcohol had taken place as the primary reaction and that secondary dehydrogenation had formed acetaldehyde.

Several patents have been granted for the hydration of olefins under

[64] Francis and Kleinschmidt, *Proc. 10th Ann. Meeting Am. Pet. Inst.* **III**, 93 (1930), New York.
[57] Wibaut and Diekmann, *Proc. Acad. Sci. Amsterdam* **26**, 321-8 (1923); *also compare* U. S. Pat. 1,497,817 (1924) Wells, assr. to Hunt.

conditions which have been shown to be favorable from a thermodynamic standpoint. To indicate the similarity of the operating conditions which are claimed these will be reviewed individually.

In order that condensates high in alcohol may be obtained, operation with a low steam to ethylene ratio has been claimed despite the difficulties that are likely to arise from polymerization of the olefin. Ethanol is formed by passing a mixture containing 5 to 10 volumes of ethylene per volume of steam over catalysts of thoria or phosphoric acid deposited on charcoal at temperatures of 400° to 500° C. and pressures of 25 to 200 atmospheres. High space velocities of 10,000 to 50,000 volumes of reactants (at normal temperature and pressure) per volume of catalyst per hour are used and may account for the presumable freedom from polymerization troubles. Examples show that with a gas containing equal proportions of steam and ethylene a liquid condensate containing 20 per cent alcohol may be obtained, and that by using a 1 to 5 ratio of steam to ethylene a 50 to 60 per cent alcohol solution is formed.[65]

In contemplating the use of high ratios of steam to olefin in vapor phase hydrations for the purpose of restricting olefin polymerization, sight must not be lost of the fact that excessive steam ratios may impair catalyst activity by flooding the active surface with water molecules. The net effect of such an occurrence would be to prevent olefin molecules from reaching the surface and becoming activated. It has been recognized that the adsorption of the product of a reaction at the catalyst surface may slow down reaction, and it is not unreasonable to suppose that a reactant may have a similar effect. For this reason a mean should be struck between high ratios of steam to prevent polymerization and low ratios to prevent loss of catalyst activity.

By mixing that fraction of the gases resulting from the cracking of petroleum oils which is not liquefied at a pressure of 100 pounds per square inch at room temperature with about four volumes of steam and passing the mixture over catalysts such as aluminium oxide, kaolin, etc., at a temperature of 300° to 450° C. and a pressure of the order of 100 pounds per square inch, it is claimed [66] that a mixture consisting mostly of butyl and amyl alcohols with smaller amounts of hexyl alcohols and some propanol may be produced. Yields as high as 80 per cent of the theory are claimed, but as no indication is given of what the theoretical yields or the actual yields are, it is difficult to evaluate the importance of this patent. Since the dilution with steam is not high, it is necessary for the process to operate at such low pressures as 100 pounds per square inch, to prevent polymerization of the higher olefins present, such as butene, pentene, and hexene, which is quite pronounced at the temperature of operation particularly when the olefins are under pressure. The statement that good yields are obtainable at atmospheric pressure at temperatures, presumably,

[65] Brit. Pat. 308,859 (1928) Slade, assr. to Imperial Chemical Industries, Ltd.
[66] U. S. Pat. 1,738,785 (1929) McKee and Burke, assrs. to Brown and Odell.

of 300° C. or above, is difficult to reconcile with the thermodynamic calculations available in regard to this type of reaction, which show that either high pressures or low temperatures are necessary for the hydration of olefins in the vapor phase.

Claims have been made for the hydration of olefins, including olefins with two or more double bonds, in the vapor phase and in the presence of catalysts as a metal of the platinum group, gold, silver, copper, iron, nickel, cobalt, chromium, tantalum, vanadium, tungsten, molybdenum, or manganese or compounds.[67] Ethylene and steam may be passed over platinum on pumice at 150° C., copper phosphate on porous stone at 155° C., or tungstic acid and ferric oxide on silica gel, reduced with hydrogen at 450° C., at 300° C., at ordinary or raised pressure and at space velocities of 2.5 to 6.7 cc. of gas per hour per cc. catalyst. Propene and steam may be passed over tungstic acid and copper oxide on active carbon at 300° C.

The difficulties attending the catalytic vapor phase hydration of olefins, while not apparent from the claims made in the patents which have been obtained for such processes, are serious and numerous. Aside from those already mentioned, the difficulties of separating the alcohol from the dilute liquid condensate by distillation and of purifying the alcohols from hydrocarbon polymers by a process of chlorination or selective absorption must be overcome. In view of the success that has attended the hydration of olefins, particularly those higher than ethylene, by means of absorption in sulfuric acid followed by dilution and distillation, it is probable that direct hydration processes at the present stage of the art will be unable to compete as long as cheap sulfuric acid is available.

Absorption of olefins in sulfuric acid of various strengths has an added advantage in that valuable ethylating compounds may be formed which may be used directly in the production of esters.[68] Thus diethyl sulfate of high purity may be obtained by reacting ethylene with 66° Bé sulfuric acid and used with great success for the ethylation of either the hydroxyl or amino groups of organic compounds.[69] It is possible also to oxidize the alkyl sulfuric acid compounds directly with air or nitric acid to form ketones or aldehydes.[70]

One of the most convincing arguments against the further development of fermentation ethanol plants is the advent of synthetic ethanol. As far back as 1921 plants were erected in Germany for the synthesis of ethanol from hydrocarbons but were not at that time very successful. Processes for the production of the synthetic product have been developed in Europe to a commercial scale while at least two American chemical companies have carried the process beyond the experimental stage. A permit was recently granted by the Commissioner of Prohibition to conduct an experi-

[67] Brit. Pat. 335,551 (1930) Elkington, assr. to N. V. de Bataafsche Petr. Maatsch; *Rev. Petrol.* 1931, 115.
[68] U. S. Pats. 1,365,050 (1920); 1,365,052 (1920) Ellis and Cohn.
[69] Curme and Curme, *Chem. Met. Eng.* 25, 957-9 (1921).
[70] U. S. Pat. 1,418,368 (1922) and U. S. Pat. 1,450,493 (1923) Ellis.

mental semi-plant scale run at the factory of one of these companies and 48,000 proof gallons of ethanol was made. The test runs were successful and the Carbide and Carbon Chemical Co. has erected a larger plant with a capacity to produce from 8,000,000 to 10,000,000 gallons of alcohol per year. Further proof that the problem of alcohol production by the hydration of olefins of low molecular weight has been satisfactorily solved on this continent is implied in a recent Government communication.[71] A process developed by the National Research Council at Ottawa is estimated to be capable of yielding 10,000,000 gallons of industrial alcohol per year from the waste gases of the Turner Valley field in Alberta. No public disclosures of the process have been made. Synthetic ethanol may be made from ethylene derived from a number of sources but it is probable that only sources giving a fairly high concentration of ethylene with good purity will be used.

In the plant mentioned above ethylene is obtained from Gyro cracking gas. The gas is compressed and refrigerated to separate the unsaturates and these are separated from each other by fractionation. Ethylene of high purity is thus obtained. The use of pure ethylene has contributed largely to the success of the process, earlier processes having been handicapped by the use of gas containing ethylene rather than the pure material. The impurities in the gases employed by the earlier processes consumed sulfuric acid by absorption in it and made recovery of spent acid difficult and unsatisfactory. Besides this source of loss some of the acid was reduced to SO_2 during concentration, increasing corrosion and constituting a nuisance. The success of the synthetic ethanol process on a commercial scale has depended quite largely upon the conservation and efficient recovery of the sulfuric acid.

One of the major restrictions to the sulfuric acid method of hydration has been the cost of reconcentrating the sulfuric acid. The necessity for this reconcentration is brought about by the fact that the strong acid used for absorption of the olefin must be diluted prior to the distillation of the alcohol from the solution. In locations where the dilute acid may be used in conjunction with the production of synthetic ammonia for the formation of ammonium sulfate fertilizers, the hydration operation may be made more profitable by this outlet for the spent acid.

Besides ethanol, large quantities of ethyl ether are produced by the sulfuric acid absorption process from ethylene. In the hydration of ethylene by this method the relative proportions of alcohol and ether obtained are determined by the temperature and concentration of the sulfuric acid solution at the hydration and recovery stage. The more dilute the acid, the higher the proportion of alcohol formed and vice versa. This same process has been applied to the formation of isopropyl ether from propene and this product is now available in tank car lots.

[71] *U. S. Dept. Commerce, World Trade Notes on Chemicals and Allied Products*, **5**, No. 11, article 22, 1931.

The hydration of the higher olefins, such as the butenes and pentenes, by the sulfuric acid absorption process has been commercially practiced for a number of years in this country. In the case of the higher olefins, a more dilute acid may be used for the absorption. Consequently acid reconcentration does not present the difficulties that are present in the case of the lower olefins where a more concentrated acid must be used.

A source of interest in the production of large quantities of cheap alcohols higher than ethanol aside from their use as solvents, is to be found in their use as blending agents in the production of motor fuel from mixtures of methanol and gasoline. Methanol is known to impart very desirable knock-suppressing properties to gasolines but is not sufficiently miscible for use directly. Higher alcohols have the property of acting as blending agents and relatively small additions permit the production of perfectly mixed methanol-gasoline motor fuels. The tremendous quantities of higher alcohols which would be available by the utilization of the olefin content alone of waste refinery gases are a potential source of cheap aldehydes and ketones and of compounds that may be derived from these.

In conclusion it may be said that the vapor phase hydration of olefins under pressure to form alcohols does not appear promising because of the major difficulties involved, notwithstanding the rather favorable theoretical possibility. On the other hand, considerable evidence has been amassed and a number of patents issued to show that hydration of olefins in solution is a commercial possibility. This early material has been very carefully collected and summarized by Brooks.[73]

It was reported in 1922 that the cost of producing synthetic ethanol in England was 30 cents per gallon.[72a] The cost of producing ethanol from ethylene in this country was estimated in 1930 to be about 35 cents per gallon [72b] and in 1931 to be about 16 to 18 cents per gallon.[72c] The net cost of producing fermentation ethanol may be assumed to vary from this low figure of 16 to 18 cents per gallon up to 25 to 40 cents per gallon depending on raw material costs.

Miscellaneous Reactions

The vapor phase dehydration of an alcohol under high pressure tends to shift the reaction toward production of an ether rather than an olefin,[74] according to the reaction:

$$2C_2H_5OH = (C_2H_5)_2O + H_2O.$$
ethanol   ethyl ether
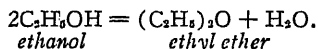
This fact suggests a stepwise mechanism for the reaction in which one molecule of ethanol is dehydrated to an olefin followed by the reaction between the olefin and another molecule of ethanol to form ethyl ether:

[73] Brooks, "The Manufacture of Alcohols from Hydrocarbons with Particular Reference to Petroleum as a Raw Material," *Chem. Rev.* 2, 369-435 (1926).
[72] a. Editorial, *J. Soc. Chem. Ind.* 41, 189R (1922); b. Watson, *Chem. Met. Eng.* 37, 160 (1930); c. Partridge, *Ind. Eng. Chem.* 23, 489 (1931).
[74] Ipatiew, *Ber.* 37, 2986 (1904); 58, 4-12 (1925).

$$C_2H_5OH = C_2H_4 + H_2O$$
$$C_2H_5OH + C_2H_4 = (C_2H_5)_2O.$$
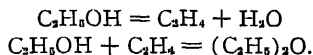
Pressure is effective in directing the latter reaction because it occurs with a decrease in volume whereas the dehydration reaction is accompanied by doubling in volume. Data in regard to the reaction of ethylene with ethanol to form ethyl ether are not available and no statement can be made regarding the occurrence of this reaction.

Similar reactions, however, involving the addition of an olefin to an oxygen containing organic molecule, have been proposed in a number of other cases. Thus, ethylene and acetone are made to react to form propyl methyl ketone:[75]

$$C_2H_4 + CH_3COCH_3 = CH_3COC_3H_7.$$
ethylene   acetone   propyl methyl ketone
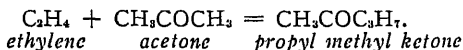
Since the reaction occurs with a decrease in volume of two to one, it will be favorably affected by high pressures. In operation, temperatures of 250° to 550° C., pressures of over 50 atmospheres, and hydrogenating-dehydrogenating catalysts as zinc and chromium oxides or zinc chlorides are claimed. No yields are mentioned in the examples that are given.

By the use of pressure and the proper catalysts it is possible to dehydrate ethanol to form butanol,[76] according to the reaction:

$$2C_2H_5OH = C_4H_9OH + H_2O.$$
ethanol   n-butanol
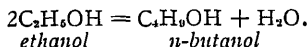
By a similar mechanism to that proposed for the formation of ethyl ether by dehydration of ethanol, it is possible that the reaction occurs stepwise with the intermediate dehydration of one ethanol molecule to form ethylene which then reacts with another ethanol molecule to form butanol. It is thus possible that higher alcohols may be built up by the reaction of olefins with the lower alcohols. Mixed oxide type of catalysts are used in the process of a nature similar to those which have been found effective in alcohol synthesis from hydrogen and carbon monoxide. It should be noted here that catalysts which promote the union of carbon atoms must be used, and since potassium oxide promoted catalysts composed of mixtures of zinc, copper, or chromium oxides have been found to be effective in the synthesis of higher alcohols, such catalysts should be useful in promoting the addition of olefins to alcohols or other oxygenated organic molecules.[77]

Although constituting a liquid phase reaction in which sulfuric acid is used as a catalyst, the direct esterification of organic acids such as acetic by addition of olefins presents some interesting phases of the usefulness of high pressure as a tool in organic synthesis. Thus, the production of

[75] U. S. Pat. 1,757,830 (1930) Brown to Commercial Solvents Corp.
[76] U. S. Pat. 1,708,460 (1928); Brit. Pat. 312,345 (1928) to E. I. duPont de Nemours & Co., Inc.; Brit. Pat. 336,811 (1930) Elkington, assr. to N. V. de Baatsch. Pet. Maats.
[77] a. D. S. Cryder, Thesis for D.Sc. at Massachusetts Institute of Technology 1930 for details of catalysts; b. Lewis and Frolich, *Ind. Eng. Chem.* 20, 354 (1928); c. Frolich and Cryder, *ibid.* 22, 1051 (1930).

an ester with an olefin as a raw material ordinarily involves three steps. (a) Formation of alkyl sulfuric acid ester; (b) formation of the alcohol by hydrolysis of this ester; (c) esterification of the alcohol with an organic acid, as acetic, usually in the presence of sulfuric acid. These steps involve the addition of water in (b) and the removal of water in (c), to give a net effect involving only organic acid and olefin:

$$C_3H_6 + CH_3COOH = CH_3COOC_3H_7.$$
propene   *acetic acid*   *propyl acetate*
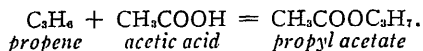
The fact that the reaction occurs with a decrease in volume of two to one makes the application of pressure of great benefit in driving the reaction to the right. Although no thermodynamic data are available with which to calculate free energy changes for reactions of this nature, some available data on the reaction itself show that it may be made to occur successfully. Thus by reacting the olefins and acetic acid in approximately equimolal concentrations at a total pressure of about 50 atmospheres and a temperature of 150° C. over zinc chloride as a catalyst, it has been possible to produce propyl and butyl acetates with 25 to 27 per cent conversions of acetic acid.[78]

The direct synthesis method for the formation of esters was tried a number of years ago but only the higher olefins were experimented with. Behal and Desgrez [79] produced heptyl acetate by heating heptene and acetic acid in an autoclave at 300° C. Pentene and acetic acid react at ordinary temperatures in the presence of zinc chloride to form esters. Considerable of the olefin, however, is lost by polymerization.[80] It is possible also to dissolve olefins in acetic acid and then add sulfuric acid to catalyze the reaction to form esters.[81] Trichloracetic acid is sufficiently active not to require a catalyst for the reaction and by heating pentene and trichloracetic acid in a sealed tube at 100° C. for a matter of hours, Nernst claimed to have obtained a yield of 88 per cent of available ester.[81c]

One of the greatest difficulties with direct esterification processes has been the tendency for the olefins to polymerize at the temperatures and in the presence of the catalysts used in the process. Energetic reagents such as anhydrous zinc chloride, ferric chloride, sulfur chloride, aluminum chloride or bromide; such substances as fullers earth; forms of energy as light, heat, silent electric discharge; and the alkali or alkali earth metals are all known to affect greatly the polymerization of olefins.

Whereas ethylene requires a fairly high temperature for polymerization even in the presence of most of the catalysts mentioned above, the higher olefins as propene, butene, etc., are more reactive and polymerize very readily. Sulfuric acid tends to cause polymerization of the olefins to higher

[78] Brezinski. Graduate Thesis, Massachusetts Institute of Technology Library.
[79] Behal and Desgrez, *Compt. rend.* 114, 676 (1892).
[80] Brooks, "Non-Benzonoid Hydrocarbons" (1922), The Chemical Catalog Co.
[81] a. Bertrom and Walbaum, *J. prakt. Chem.* 49. 7 (1894); b. Brit. Pat. 334.228 (1929); Can. Pat. 305.196 (1930) Woolcock assr. to Imperial Chemical Industries, Ltd.; c. Nernst, "Physical Chemistry," 5th. Ed., p. 538.

boiling, more viscous, non-reactive polymers, the formation of which represents a loss of raw material and constitutes one of the objectionable features of the sulfuric acid processes. The use of zinc chloride, however, in an anhydrous form with anhydrous reactants makes it possible to esterify acetic acid with propene and butene without loss to polymers.[78]

The economic utility of the direct esterification process depends, of course, upon cheap acetic acid (if acetates are being sought). For the process to compete with the present method for esterification which uses calcium acetate of about 85 per cent purity a source of cheap acetic acid will be necessary. Although a price considerably lower than the present quoted price for acetic acid is necessary, it seems possible that it could be made from acetylene at a satisfactory price.[82]

Since olefins may be added to alcohols, ketones, and acids directly, it is probable that reaction could be effected between olefins and esters to give higher esters as exemplified by the reaction:

$$C_2H_4 + CH_3COOC_2H_5 = CH_3COOC_4H_9.$$
$$\textit{ethylene} \quad \textit{ethyl acetate} \quad \textit{butyl acetate}$$

Pressure would be effective and catalysts similar to those used in the other reactions involving carbon to carbon linkages would probably be the most useful.

Olefins readily form addition products[83] with such substances as hydrogen chloride,[a] hypochlorous acid,[b] chlorine,[c] nitrogen tetroxide,[d] sulfur dioxide,[e] etc. Most of the reactions of this type are, however, conducted in the liquid phase because of greater ease of control of operating conditions.

References may be found in the literature to attempts made for the purpose of reacting ethylene in a variety of other ways to obtain useful products. Condensation and oxidation products are claimed to be formed when ethylene mixed with steam, ammonia, or hydrogen sulfide is passed over catalysts at high temperatures.[83f] Unsuccessful attempts have been made to obtain acetone by reacting ethylene with hydrogen and carbon monoxide in a molal ratio of $1:2.5:1$, respectively, at 300° C. and 150 to 250 atmospheres pressure in the presence of a basic zinc chromate catalyst. In this case methanol was formed, a portion of the ethylene polymerized, and a portion was reduced to ethane.[83g] No acetone was formed.

ACETYLENE

Acetylene is most generally produced by the reaction of water on calcium carbide which has been formed in electric furnaces from coke and

[82] *Compare* Partridge, *Ind. Eng. Chem.* **23**, 482-98 (1931).
[83] a. Coffin, Sutherland, and Maass, *Can. J. Research* **2**, 267-78 (1930); *Chem. Abstracts* **22**, 2139-40; b. Curme and Young, *Chem. Met. Eng.* **25**, 1091-2 (1921); c. Curme, *Chem. Met. Eng.* **25**, 999-1000 (1921); *Chem. Abstracts* **16**, 553; d. Schaarschmidt and Hofmeier, *Ber.* **58B**, 1047-54 (1925); *Chem. Abstracts* **19**, 942; e. Mathews and Elder, Brit. Pat. 11,635 (1914); f. Brit. Pat. 109,983, Stuer and Grob, assrs. to Chem. Fab. Rhenia; g. Brit. Pats. 247,932; 247,178 (1926) Patart; Nash, *J. Soc. Chem. Ind.* **45**, 876 (1926); Brit. Pat. 255,127 (1926) Badische Anilin u. Soda Fabrik.

lime. This method is dependent for its industrial success on sources of cheap electric power and as a result the manufacture of acetylene and its utilization as an organic intermediate is usually centered at points where electric energy is cheap and available in large quantities.

The reaction of water on calcium carbide:

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2$$
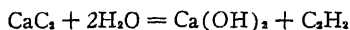
is accompanied by violent evolution of the gas and the liberation of considerable quantities of heat. To prevent polymerization reactions and other decompositions brought about if the temperature gets too high, it is necessary to employ special apparatus for conducting the liberation of acetylene from the carbide. For certain catalytic reactions involved in the utilization of the acetylene it is also essential that impurities such as sulfur, phosphorus, arsenic, and silicon derivatives be removed to prevent catalyst poisoning.[84]

Considerable attention has recently been attracted to the possibility of producing cheap acetylene by cracking methane in the electric arc. A consideration of the free energy data for acetylene [85] shows that it is stable at temperatures of about 3000° C., tends to polymerize at temperatures in the neighborhood of 1000° C., and although thermodynamically unstable at room temperature has a reactivity sufficiently low to prevent polymerization and decomposition at a measurable rate. Thus, in forming acetylene by electric arc cracking of methane it becomes necessary to use short times of contact and to cool exceedingly rapidly to temperatures below 1000° C., with operation at reduced pressure or in the presence of diluent hydrogen.

A number of patents have been issued claiming various methods for the operation of this process. Krauch [86] states that it is possible by this method to convert methane almost completely into acetylene with an energy efficiency of 35 to 40 per cent.

Cost figures on acetylene production by this method are not directly available but may be approximated from some of the data on energy consumption. With no attempt at high energy efficiencies and with an obviously inefficient arc an energy consumption of 3400 K.W.H. per thousand cubic feet of acetylene has been obtained.[87] An energy consumption of 822 K.W.H. per thousand cubic feet of acetylene has been reported.[88] The basis for the efficiency reported by Krauch [86] is a yield of 85 to 90 liters of acetylene per K.W.H. of electrical energy. Conversion to English units shows that an energy consumption of only 315 to

[84] For the preparation and properties of acetylene *see* a. Lewes, "Acetylene," New York, Macmillan Co., 1900; b. Leeds and Butterfield, "Acetylene, Its Generation and Use," London, Griffin and Co., Ltd., 1910; c. Vogel, "Das Azetylen," Leipzig, Spamen, 1911; d. Muhlert and Drews, "Technische Gase," Leipzig, S. Hirzel, 1928, p. 18, 62; e. Taussig, "Die Industrie des Kalziumkarbides," Halle, W. Knapp, 1930.
[85] Francis, *Ind. Eng. Chem.* 20, 227 (1928).
[86] *Proc. 2nd. Intl. Conf. on Bituminous Coal*, 1928; 32-47, Carnegie Inst. Tech., Pittsburgh.
[87] Frolich, White, Uhrmacher and Tufts, *Ind. Eng. Chem.* 22, 23 (1930).
[88] Snader, *Petr. Times*, March 8, 1930, p. 405.

350 K.W.H. per thousand cubic feet of acetylene is required. A Schönherr arc oven was operated with a mixture containing one to 1½ volumes of hydrogen per volume of methane, to obtain the efficiency reported.

Small electrically heated tungsten coils have also been used experimentally for the formation of acetylene by cracking methane.[89] At 3000° C. and with a time of contact of 0.0004 second a conversion of 86 per cent has been reported as obtainable from coke-oven gas containing 25.5 per cent methane. The results of this experimental work indicate that higher yields are possible by the electric arc method.

A gas containing several per cent of acetylene may be formed by passing methane through gas flames at temperatures of about 900° C. About half as much methane is used for heating as is treated but other unsaturated hydrocarbons as well as certain polymerized compounds are formed at the same time.[90] The dilute acetylene may be recovered by scrubbing or used directly to form acetaldehyde. Acetone furnishes a suitable selective absorbent for acetylene which may be recovered readily in a pure form. Selective absorption on active charcoal furnishes another suitable method for the separation of acetylene from mixtures containing methane, hydrogen, and nitrogen.

The ordinary method of hydrating acetylene to acetaldehyde by passing it through an acid solution containing salts of mercury as catalysts has the objectionable features of sludge formation and consequent cost of regeneration of catalyst. This liquid phase process has an advantage in that dilute acetylene containing gases may be used. Thus, gas obtained from "cracking" of methane in an electric arc or by passing through incandescent coke, and containing 2 to 10 per cent of acetylene may be used in the production of acetaldehyde by scrubbing with a solution containing 10 to 20 per cent sulfuric acid, 7 per cent ferric sulfate and 1 per cent mercuric sulfate. The unreacted methane may then be recirculated.[91] It is also possible to control the temperature of liquid phase reactions better. It is claimed to be possible to control the temperature of this reaction by regulating the inflow of acetylene so that the heat of reaction is equal or less than the heat of evaporation.[92] The temperature may also be controlled by limiting the amount of catalyst present in the acid solution.[93a] Although methods have been proposed and tried with the intent of overcoming the objectionable features, the process is still not free from difficulties. As a consequence, interest has been manifested in the direct vapor phase conversion of acetylene to oxygen containing compounds by oxidation, hydration, or a combination of the two, although it is doubtful

[89] a. Peters and Meyer, *Brennstoff. Chem.* 10, 108, 324 (1929); *see also* b. Peters and Pranschke, *Brennstoff. Chem.* 11, 239-247 (1930); c. Rudder and Biedermann, *Compt. rend.* 190, 1194-6 (1930); *Bull. soc. chim.* (4) 47, 704-30 (1930); d. Brit. Pat. 332,731 (1930) Winter, Hull, and Fergusson, assrs. to Imperial Chemical Industries. Ltd.
[90] Brit. Pat. 264,845 (1928) I. G. Farbenindustrie, A.G.
[91] a. Brit. Pat. 302,515 (1928) Hirst and Imperial Chemical Industries, Ltd.; b. French Pat. 671,285 (1929) I. G. Farbenindustrie, A.G.
[92] French Pat. 678,745 (1929) Holzverkohlungs Ind. A.G.
[93] a. U. S. Pat. 1,738,649 (1929) Hand, Bartram, and Maude to Rubber Service Labs. Co.; b. Brit. Pat. 288,707 (1927) Walter, assr. to Verein f. Chem. Ind.

if such processes have been perfected to a point where they are able to compete with liquid phase processes.

The liquid phase process employing an acid solution and mercury salts is also sufficiently flexible to enable other reactions to be conducted, suggestions of which may be found in the patent literature.[93b] Thus, ethylidine diacetate, or dipropionate may be obtained by passing acetylene and acetic or propionic acid vapors into the aqueous acid containing mercury salts. The vinyl ester of trichloracetic is obtained when trichloracetic acid is used in a similar manner. Acetylene and isobutanol vapor passed into a suspension of mercuric sulfate in the alcohol form ethylidene-diisobutyl ether. Similarly, the use of ethylene glycol gives rise to ethylene ethylidine ether.

Ethylidene diacetate is being used as a source for the manufacture of acetic anhydride. The reaction between acetic acid vapor and acetylene is used for the production of the ethylidene diacetate, which is subsequently decomposed into acetic anhydride and acetaldehyde.[82] The acetaldehyde thus released may again be oxidized to acetic acid.

As has been stated in the case of ethylene, the catalytic oxidation of unsaturated hydrocarbons is complicated by the fact that such substances are somewhat sensitive to the action of hydrolyzing agents. The presence, therefore, of even small amounts of water in the oxidizing gases makes it difficult to determine the exact mechanism of the process, i.e., whether the primary reaction consists of oxidation, hydration, or simultaneous oxidation and hydration. The same situation is met with again in the catalytic oxidation of acetylene and is further complicated by the fact that the primary products of hydrolysis and oxidation tend to undergo a variety of different secondary reactions.

The primary products of the oxidation and hydrolysis of acetylene may be assumed to be respectively glyoxal and acetaldehyde:

$$(a) \quad \begin{matrix} CH \\ ||| \\ CH \end{matrix} + \begin{matrix} O \\ | \\ O \end{matrix} \longrightarrow \begin{matrix} OCH \\ | \\ OCH \end{matrix}$$

$$(b) \quad \begin{matrix} CH \\ ||| \\ CH \end{matrix} + \begin{matrix} H \\ | \\ OH \end{matrix} \longrightarrow \begin{matrix} CH_2 \\ || \\ CH.OH \end{matrix} \longrightarrow \begin{matrix} CH_3 \\ | \\ OCH. \end{matrix}$$
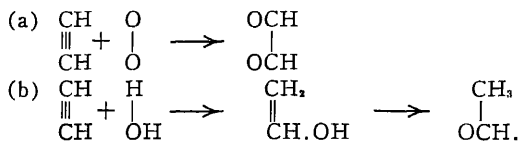
Thus, for example, when (a) air containing oxygen and about one per cent ozone is passed through water and then mixed with one and a half volumes of acetylene in a large vessel, glyoxal is observed to condense on the walls of the vessel.[94] In the hydrolysis (b) a liter flask was filled with acetylene gas and a small quantity of water containing a suspension of finely powdered mercury bromide was then added. After shaking and warming on the water bath for some days, the contents of the flask were carefully distilled into ether saturated with ammonia when aldehyde-ammonia was precipitated.[95]

[94] Ger. Pat. 324,202 (1916) Wohl and Braunig; *also Chem. Ztg.* **44**, 157 (1920). Oxidation to glyoxal has also been observed to take place in solution. K. Kindler, *Ber.* **54**, 647 (1921).
[95] Kutscheroff, *Ber.* **14**, 1540 (1881). *Compare also Ber.* **17**, 13 (1884).

When acetylene is exploded with less than an equimolar volume of oxygen present, a portion of the acetylene is burnt to carbon monoxide and hydrogen presumably through the intermediate, unstable $C_2H_2O_2$ molecule and the remainder decomposed to carbon and hydrogen. Thus:

$$C_2H_2 + O_2 = C_2H_2O_2 = 2CO + H_2$$
$$C_2H_2 = 2C + H_2.$$
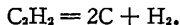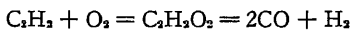
Since no water is formed under these circumstances, the process differs from that wherein ethylene is involved. Also, no methane appears in the products. From these results it may be concluded that no monohydroxy acetylene compound is formed as has been postulated for other hydrocarbons.[96]

In order to isolate intermediate oxidation products of acetylene it is necessary that the oxidation be at a lower temperature than that which prevails in explosions. From the results obtained from experiments conducted at 250° to 350° C. with such mixtures of acetylene and oxygen as 2:1, 1:1, 2:3, 1:2, 1:3, Bone and Andrew[97] postulated a mechanism for the slow oxidation as involving the formation of an unstable product, $C_2H_2O_2$, $(HOC \equiv COH)$, which decomposed directly to formaldehyde and carbon monoxide. They were able to identify formaldehyde, formic acid, and a polyglycolide, $(C_2H_2O_2)_x$, and to prove that carbon monoxide and formaldehyde arise simultaneously at an early stage of the process; and that formation of formaldehyde precedes that of water. These results seem to support the mechanism proposed very well. In common with the findings of Dixon[98] on the explosion of acetylene-oxygen mixture, these workers found that an excess of oxygen above an equimolal volume retarded the reaction. Recirculation of an acetylene-oxygen mixture through a tube packed with porcelain and maintained at a temperature of 380° C., with continuous removal of oxygenated products by condensation and scrubbing, showed that of the acetylene decomposed the carbon was distributed 44 per cent to carbon dioxide, 39 per cent to carbon monoxide, 17 per cent to formaldehyde, and the hydrogen 34 per cent to formaldehyde, 61 per cent to water, and 5 per cent appeared as such.

The wholly homogeneous character of the oxidation of acetylene has recently been demonstrated and evidence accumulated to support a chain type of reaction.[99] The reaction thus appears to be similar to that of ethylene oxidation in regard to kinetics.[28] At temperatures of 250° to 315° C. the oxidation proceeded through the stages of glyoxal, formaldehyde, formic acid, carbon dioxide and water. All of the reaction products were isolated and a mechanism, similar to that shown here was postulated:

$$\begin{array}{c} CHO \\ | \\ CHO \end{array} \Big\langle \begin{array}{l} CO + H_2CO \\ 2CO + H_2 \end{array} \xrightarrow{+O_2} HCOOH \xrightarrow{+O_2} \begin{array}{l} CO_2 + H_2O. \\ CO + H_2O \end{array}$$
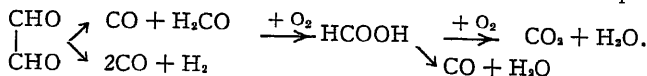
[96] a. Bone, *Nature* 124, 839-40 (1929); b. Bone and Cain, *Trans. Chem. Soc.* 71, 26 (1897).
[97] Bone and Andrews, *J. Chem. Soc.* 87, 1232-48 (1905).
[98] Dixon, *Phil. Trans.* 184, 183 (1893).
[99] Kistiakowsky and Lenher, *Nature* 124, 761 (1929), (announcement); *J. Am. Chem. Soc.* 52, 3785 (1930).

The rate of the reaction is abnormal, being proportional to the square of the acetylene concentration and almost independent of the oxygen concentration. The rate of the homogeneous reaction is reduced manyfold by the presence of large surfaces and a heterogeneous type of reaction induced giving reaction to carbon dioxide and water. The rate of this heterogeneous reaction is proportional to the product of the acetylene and oxygen concentrations.

Most of the early work on the catalytic oxidation of acetylene resulted in the formation of complete combustion products. Thus, in the presence of palladianized asbestos at temperatures above 339° C. carbon dioxide and water were formed if sufficient oxygen was present and carbon monoxide and water if the oxygen was not sufficient for the complete combustion. The hydrogen and carbon were oxidized simultaneously.[100] When pure acetylene was passed over palladianized copper oxide, however, water began to form at temperatures as low as 225° to 230° C. but no carbon dioxide. Even at temperatures as high as 400° C. carbon was deposited and the amount of water formed was always in excess of the carbon dioxide.[101]

The effect of different metal catalysts upon the oxidation of acetylene has been made the subject of preliminary investigation by Bellamy,[102] who observed that the complete oxidation of the substance was progressively accelerated by iron, copper and platinum. He found that a hot spiral of platinum or silver detonated a mixture of acetylene and air but did not become incandescent. A copper spiral, however, when treated in the same way became brilliantly incandescent and eventually ignited the mixture. A spiral of iron acted in the same way but the incandescence was more difficult to obtain.

In the presence of nitrogen oxides the reaction between acetylene and oxygen proceeds as a homogeneous reaction catalyzed by NO_2.[103] Trimeric glyoxal was found to be the major product of the reaction. Formaldehyde, formic acid, carbon oxides, hydrogen, and water constituted the remainder of the product. Under the conditions of the experiments and at temperatures below 260° C. acetylene does not react with NO.

Preliminary investigations of the hydrolysis of acetylene at temperatures of about 400° C. in the presence of catalysts such as carbon,[104a] porous porcelain[104b] and aluminum oxide[105] have been described by Desgrez, Bone and Tschitschibabin. The latter also experimented with the oxides of zinc, iron, and nickel at 300° C. and was able to show that the products of hydrolysis invariably represent mixtures which vary greatly in their composition, the exact nature of the mixture depending

[100] Phillips, *Z. anorg. Chem.* **6**, 212 (1894).
[101] Campbell, *Am. Chem. J.* **17**, 681 (1896).
[102] *Compt. rend.* **100**, 1460-1 (1885).
[103] Lenher, *J. Am. Chem. Soc.* **53**, 2962-7 (1931).
[104] a. Desgrez, *Ann. chim. phys.* (7) **3**, 209 (1894); b. Bone and Andrews, *J. Chem. Soc.* **87**, 1244 (1905).
[105] Bone, *Proc. Chem. Soc.* **21**, 220-1 (1905); Tschitschibabin, *J. Russ. Phys. Chem. Soc.* **47**, 703 (1915).

upon the catalyst and the temperature of the reaction. For example, when acetylene and steam were passed over alumina or ferric or chromic oxides at 400° to 425° C. the product was found to consist of a mixture of saturated and unsaturated aliphatic and aromatic hydrocarbons. When the same gases were passed over the oxides of zinc, iron, or nickel at 300° C. acetaldehyde was formed, but this condensed rapidly with loss of water to give crotonaldehyde.[106]

In all of this early work the general observation was made that the successful operation of the process was greatly interfered with by the rapid deterioration of the catalyst. This seemed to depend in part upon impurities present in the acetylene (phosphorus and its compounds being particularly potent poisons) and also upon the deposit of carbon on the surface of the catalyst due to decomposition reactions. When metal oxides or compounds such as, for example, molybdic acid were used, deterioration appeared to be due at least in part to the partial reduction of these compounds. In most of these cases the activity of the catalyst was restored [107] by heating it in a current of air at high temperatures (600° C.).

The fact that acetylene is vigorously acted on by such metals as copper, nickel, platinum, cobalt, iron, etc., at temperatures of from 150° to 250° C. with resultant formation of polymers, carbon, hydrogen, olefins, and low molecular weight paraffins [108] must of necessity be considered in the use of such metals as catalysts for the oxidation or hydration reaction in the vapor phase. However, unless very low concentrations of oxygen are used, metallic catalysts would be coated with a surface film of oxide which would blanket the action of the metal. Acetylene is capable of undergoing a variety of pyrogenic condensations when heated with or without the presence of a catalyst and the reader should refer for data along these lines to the early work of Berthelot [109] and the more recent work of Meyer [110] and Zelensky.[111] The effect of catalysts upon condensations of this type has been the subject of investigation by Alexander,[112] Erdmann and Köthner,[113] Sabatier and Senderens [114] and Tiede and Jenisch.[115] The behavior of acetylene in the presence of methane and its homologs has been studied by Heinemann.[116]

A patent, the specifications of which are very broad, describes the preparation of acetaldehyde and also of various other substances by the

[106] *Compare* Berthelot, *Compt. rend.* **128**, 336 (1899).
[107] Deutsche Gold and Silber- Schwidanstalt von Rossler, Ger. Pat. 334,357 (1916); *also*, U. S. Pat. 1,244,901-2 (1917) Scheller.
[108] Green, "Industrial Catalysis," New York, Macmillan Company, 1928, p. 172-4.
[109] Berthelot, *Compt. rend.* **62**, 905 (1860); **63**, 479 and 515 (1866); *Ann. chim. phys.* (4) **9**, 445 (1866); **12**, 52 and 64 (1867); **16**, 143 and 172 (1869), etc.
[110] Meyer, *Ber.* **45**, 1609 (1912); **46**, 3183 (1913); **47**, 2765 (1914); **50**, 422 (1917); **51**, 1571 (1918); **53**, 1261 (1920), etc.
[111] Zelensky, *Compt. rend.* **177**, 882 (1923); *Ber.* **57**, 264 (1924).
[112] *Ber.* **32**, 2381 (1899).
[113] Erdmann and Köthner, *Z. angew. Chem.* **18**, 49 (1898).
[114] Sabatier and Senderens, *Compt. rend.* **130**, 250 (1900).
[115] *Brennstoff Chem.* **2**, 5 (1920).
[116] Heinemann, Ger. Pat. 294,794 (1913); 315,747 (1915); *Chem. Zentr.* 1920 (2) 187 and (4) 222.

interaction of acetylene and steam in the presence of different catalysts.[117] In contact with hot surfaces such as unglazed porcelain, acetylene unites with steam to form aldehyde even in the presence of oxygen. This reaction has been noted in the oxidation studies on acetylene and served to introduce a complication in those cases. The presence of methane in hydrolysis experiments is due largely to decomposition of acetaldehyde at the temperatures used:

$$CH_3CHO = CH_4 + CO.$$
Acetaldehyde
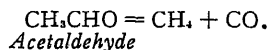
The catalysts may consist of mixtures of the oxides of iron, copper, cobalt or nickel with the oxides of aluminum, chromium, silicon or vanadium deposited in finely divided condition upon various carriers such as bog-iron ore, bauxite, etc. Alkali or alkali earth metals or magnesium compounds may be added to the contact mass and in special cases oxygen or gases containing oxygen, hydrogen sulfide, or ammonia may be added to the reacting gases. The products consist of mixtures which contain acetaldehyde, ethanol, acetic acid, and acetone along with higher aldehydes, alcohols, ketones, phenols, hydrocarbons and various derivatives containing sulfur and nitrogen. These reactions are described as taking place at temperatures ranging between 250° and 500° C. Except in certain cases, the use of metallic compounds reducible by acetylene and containing water of hydration which is retained at the temperature of the reaction, such as bog-iron ore, bauxite, and complex hydrated silicates, is restricted to such conditions as do not give complete reduction to the metal since carbon and high boiling condensation products are formed otherwise. When acetylene and steam in the ratio of 1:4 are passed over bog-iron ore at 400° to 420° C., a yield of 15 to 16 per cent of acetaldehyde is obtained together with quantities of acetone, higher aldehydes, acetic acid, unchanged acetylene, etc. With equal volumes of steam and acetylene higher boiling products are obtained including phenol, tars, etc.

Another process covering the preparations of pure acetaldehyde at temperatures below its point of decomposition has been patented.[118] According to the specifications pure acetylene need not be used in this process since what are ordinarily considered as impurities have little if any effect upon the percentage yield. The catalyst may consist of oxides or salts of mercury, copper, zinc, lead, nickel, tin, iron, aluminum, molybdenum and the like, precipitated upon a porous base such as charcoal, silica gel, etc. A gaseous mixture consisting of 200 volumes of steam to 10 volumes of acetylene when passed, for example, over activated carbon impregnated with mercuric oxide (0.5 to 1.0 per cent) gives 90 per cent acetaldehyde at 103° C. and 30 per cent at 170° C. Activated carbon impregnated with mercury gives yields increasing to 30 per cent at 250° C. and then decreas-

[117] Brit. Pat. 109,983 (1916) Stuer and Grob; *also* U.S. Pat. 1,421,745 (1922) Stuer and Grob, assrs. to The Chemical Foundation.
[118] U.S. Pat. 1,355,299 (1920) Bender

ing with increase in temperature. The same carrier impregnated with copper oxide gives 5 per cent acetaldehyde at 220° C.; 15 per cent at 250° C.; 30 per cent at 280° C. and 90 per cent at 305° C. Numerous other experimental results are described.

On the other hand, Scheller [110] goes to great length to obtain acetylene in a pure condition for reaction with steam at a temperature of 600° C. over a catalyst composed of molybdenum oxide deposited on asbestos. Despite the high temperature used a yield of 17 per cent of acetaldehyde is claimed. This may in part be attributed to the high proportion of steam used, i.e., 400 volumes steam to 15 volumes acetylene. With a 35 cm. length of catalyst a rate of one liter of this mixture per minute per sq. cm. of cross section is used.

Because of the necessity for using mixtures dilute in acetylene to avoid decomposition as well as to control the temperature of the reactions, it is possible to use gases containing rather low concentrations of acetylene instead of the pure hydrocarbon. It is claimed that passage of such gases with steam over catalyst masses containing boric or phosphoric acids or the copper, nickel, or iron salts of these acids at temperatures of 200° to 300° C. results in the formation of acetaldehyde. [120]

Alumina catalysts activated by additions of dehydrogenating catalysts, e.g., nickel oxide, copper oxide or sulfide, zinc oxide or sulfide, cobalt selenide, zinc phosphate, cadmium tungstate, mixtures of the oxides of zinc and tungsten, of cadmium and molybdenum, etc., are claimed to be superior in the formation of acetaldehyde from mixtures of steam and acetylene at 350° to 400° C. [121a] Zinc oxide catalysts may be activated in a similar way by the addition of small amounts of molybdates or molybdic acid, and are effective at 300° to 350° C. [121b]

Mixtures of acetaldehyde and acetic acid may be obtained [122] by passing acetylene (2 to 3 volumes) and air (10 volumes) mixed with a large excess of steam over the zinc, copper, nickel, or cadmium salts of vanadic, molybdic, or chromic acids deposited upon a suitable base, such as pumice, at temperatures ranging from 300° to 400° C. For example, yields of 75 to 80 per cent acetaldehyde along with 5 per cent acetic acid have been obtained by using basic zinc vanadate at 380° C. The aldehyde is separated by fractional condensation in a column and the condensed fraction which is poor in aldehyde is utilized to furnish steam for the catalytic treatment of more acetylene. The fractions rich in acetaldehyde serve for the direct recovery of the aldehyde or may be oxidized immediately to acetic acid by passage over a suitable catalyst. In this way, the process may also be applied directly to the preparation of acetic acid from acetylene.

[110] Scheller, U.S. Pat. 1,244,901 (1917); 1,244,902 (1917); Ger. Pat. 334,357 (1921).
[120] Ger. Pat. 489,360 (1926) I. G. Farbenind.
[121] a. Brit. Pat. 332,635 (1929) I. G. Farbenind. b. Brit. Pat. 334,427 (1930) Horsley, assr. to Imperial Chemical Industries, Ltd.
[122] Brit. Pat. 154,579 (1922) Wohl.

When steam is replaced by hydrogen and oxygen in the stoichiometric relations necessary to form water, the temperature at which acetaldehyde is produced from acetylene is claimed to be materially lowered. In such cases, the gaseous mixture must be diluted by the addition of an inert gas in order to avoid the possibility of explosions. The catalyst may consist of a mixture of two or more finely divided metals (nickel, copper, iron, or magnesium with some member of the platinum group) distributed on a suitable carrier. For example, the formation of 8 to 10 per cent ethyl alcohol has been claimed in one passage of a mixture of acetylene, hydrogen, oxygen, and nitrogen (in the proportion by volume of 2 : 4 : 2) over a nickel-palladium catalyst at 100° C. The ethanol which is obtained in this way may be regarded as a reduction product of acetaldehyde. After removal of the alcohol (by condensation or solution in water) the residual gases may be enriched to the correct proportions and recirculated. This patent deserves consideration since the specifications cover the direct preparation of ethanol from acetylene.[123] Another patent dealing with this transformation describes the oxidation of acetylene by use of mixtures of ozone and hydrogen but this procedure is not practical since it requires very low temperatures (i.e., the temperature of solid carbon dioxide) in order to moderate the violent reaction of the ozone.[124]

Acetylene may also be transformed directly into acetone.[125] This reaction is based upon the fact that acetic acid is known to be formed by the action of oxygen and steam upon acetylene in the presence of certain catalysts [126] and is characterized by the use of a double salt of thorium with an alkali or alkali earth metal [$Th(CO_3)_5K_6 + 10H_2O$] deposited upon a suitable carrier (burnt clay or pumice). For example, a mixture of one volume of acetylene and two to five volumes of steam is passed through tubes charged with the catalyst and heated at 350° to 450° C. The product is claimed to consist of 40 per cent acetone (calculated on the acetylene used) in addition to carbon dioxide, some carbon monoxide and methane with only slight traces of acetaldehyde, formaldehyde and an empyreumatic material. The gradual decrease in activity of the catalyst may be avoided by intermittent heating in a current of air and steam. The formation of acetone is probably through intermediately formed acetaldehyde since it has been claimed that by passing acetaldehyde and steam at the rate of 300 cc. of 30 per cent aqueous acetaldehyde solution per hour over 1 liter of catalyst at 400° C. a conversion of 93 per cent to acetone may be obtained. The use of catalysts such as oxides or other compounds of metals, the acetates of which decompose with production of acetone, deposited on aluminum rings is claimed for the process.[127] Catalysts such as alkali earth oxides, magnesium oxide or carbonate, oxides of manganese, zinc, tin, chromium, and aluminum or mixtures of these compounds are

[123] Ger. Pat. 356,175 (1922) Karo.
[124] Ger. Pat. 149,893. *Compare also* Henry, *Poggendorf's Ann.* (II) 9, 391 (1836).
[125] Brit. Pat. 192,392 (1923) Eletrizitatswerk Lonza.
[126] *Compare* Brit. Pat. 109,983 and 154,579 Stuer and Grob, assrs. to Chem. Fab. Rhenia.
[127] a. Brit. Pat. 313,897 (1928) I. G. Farbenind. b. Brit. Pat. 330,350 (1929) I. G. Farbenind.

claimed.[128]   Mixtures of zinc and aluminum are effective at 350° to 500° C.[129] in promoting the formation of acetone.

Acetic acid formed from acetylene by the successive hydration and oxidation steps:

$$HC \equiv CH + H_2O = CH_3CHO$$
$$\text{\textit{acetaldehyde}}$$
$$CH_3CHO + 1/2O_2 = CH_3COOH$$
$$\text{\textit{acetaldehyde}} \qquad \text{\textit{acetic acid}}$$
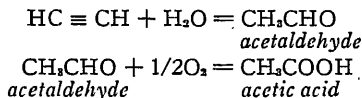
is used in the production of esters such as ethyl acetate for use as solvents. However, it is possible to form ethyl acetate directly from acetaldehyde by condensation over aluminum ethoxide.[180]   Other catalysts such as titanium ethoxide, aluminum isopropoxide, and aluminum butoxide may also be used.[181]   Such a process has considerable economic interest since it eliminates the formation of acetic acid and the necessity for using alcohol and sulfuric acid.

The action of ozone on acetylene is very violent and explosions result when the reaction is conducted in the vapor phase.   However, it is possible to study the mechanism of the reaction by carrying out the ozonization in solution.   The ozonide formed in this way is too unstable to be isolated and only by allowing a very slow decomposition to occur by slow evaporation of the solvent is it possible to isolate reaction products.   In this way, it has been found that the material remaining after evaporation of the solvent consists of a large proportion of glyoxal (81 per cent) and a small amount of formic acid (5.6 per cent).[132]   The decomposition of the ozonide of acetylene differs from that of ethylene in that the linkage of carbon to carbon is not destroyed.   The direct oxidation of acetylene with ozone, however, results in the formation of formic acid and carbon dioxide.[138]

When mixtures of acetylene and either of the oxides of carbon are passed through tubes heated to redness or are exploded with an electric spark, all of the carbon in the gaseous reactants is deposited and the hydrogen from the acetylene combines with the oxygen of the carbon oxide to form water.   Thus:

$$C_2H_2 + CO = H_2O + 3C$$
$$2C_2H_2 + CO_2 = 2H_2O + 5C.$$
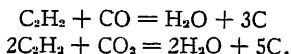
A similar reaction occurs when carbon oxides are passed over calcium carbide at a temperature of 200° to 250° C., carbon being deposited and calcium oxide being formed.[84b]   Thus:

$$CaC_2 + CO = CaO + 3C$$
$$2CaC_2 + CO_2 = 2CaO + 5C.$$
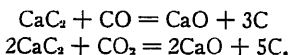
[128] Brit. Pat. 330,350 (1929) I. G. Farbenind.
[129] U.S. Pat. 1,755,193 (1930) Schlecht, assr. to I. G. Farbenind.
[130] Tischtchenko: Beilstein 4th Ed., Vol. II, p. 291.
[131] Child and Adkins, *J. Am. Chem. Soc.* 47, 798 (1925).
[132] Briner and Wunenburger, *Helv. Chim. Acta* 12, 529-53 (1929); *Chem. Abstracts* 23, 5156 (1929).
[133] Mailfert, *Compt. rend.* 94, 860 (1882).

The carbon deposits in an amorphous condition at moderate temperatures but becomes graphitized when the temperature is raised too high. These reactions have been made the basis of patent claims.

Although numerous patents have been issued for processes claiming to yield valuable oxygen-containing organic compounds by the vapor phase reaction of oxygen, water, or both, on acetylene, it may be concluded that, in general, they are not adapted to technical utilization in competition with older methods. The yields are too small and the formation of by-products too large in the processes so far developed.[184]

[184] Ullmann, "Enzyklopädie der technischen Chemie," 2nd Ed., Vol. 1, p. 95-99.

Chapter VIII

Oxidation of Petroleum Oils

Notwithstanding the fact that petroleum offers an enormous and cheap supply of raw material for organic chemical synthesis, there has been but a relatively small amount of research directed specifically toward this end. This has undoubtedly been due to the striking lack of knowledge in regard to the chemical constitution and behavior of the great number of compounds that go to make up the average petroleum oil. The petroleum industry has begun to recognize this lack of information and to feel the need for it in the development of new processes and the improvement of existing ones. As a result more is beginning to become known regarding the chemistry of petroleum [1] and this gradually enhanced knowledge is beginning to be reflected in a growing attempt to utilize this valuable material for the production of organic chemicals and intermediates rather than simply as a source of heat and power and as a lubricant.

It is interesting indeed to look into the future with these recent developments as a background and see a great new chemical industry based on petroleum as a raw material. In fact, petroleum is a source from which many of the industrially important aliphatic compounds can be made and very probably at low cost. Some of the possibilities may be enumerated as : formation of new solvents and plastics, new soaps and detergents, new flavors and perfumes, better rubber substitutes and softeners; production of fuels with better properties, of lubricants having characteristics nearer the mythical ideal; production of hydrogen and carbon monoxide for synthesis of compounds not possible of direct formation from hydrocarbons ; etc.[2]

Because of its apparent experimental simplicity, the oxidation of the higher members of the saturated and unsaturated series of hydrocarbons to produce fatty acids, fats and soaps was one of the first reactions to be studied in regard to the utilization of petroleum as an organic intermediate. Altogether, a considerable amount of work has been directed to this reaction. This work, however, has consisted to a large extent in the passing of air or oxygen through the liquid hydrocarbons with or without the

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[1] a. Washburn, Bruun and Hicks, *U. S. Bur. Standards J. Research* **2**, 467-88 (1929). b. Bruun and Hicks-Bruun, *ibid.* **5**, 933-42 (1930), etc.

[2] Products from petroleum: Hamor, *Chem. Met. Eng.* **23**, 425-34 (1920) ; Bacon, *Ind. Eng. Chem.* **15**, 888-90 (1923) ; *Bull. soc. ind. Mulhouse* **91**, 439-66 (1925) ; Norris, *Ind. Eng. Chem.* **18**, 1019-21 (1926) ; Aschan, *Chem. Ztg.* **51**, (4) (1927) ; Burrell, *Oil & Gas J.,* July 12, 1928, p. 168 *et seq.;* Weiss and Downs, *Natl. Petroleum News* **19**, No. 43, 45 (1927).

admixture of catalysts [3] and under various conditions of temperature and pressure. Such processes, although simple in operation, are open to a number of serious objections. For instance, at the point of entry of the air or oxygen the concentration of the oxidant is very high and instead of a partial oxidation occurring throughout the mass of the oil, a portion of the oil may be completely oxidized due to the local rise in temperature produced by the highly exothermic reaction. Also, even if the oxidation is uniform and only partial, the products of the oxidation are forced to remain at the reaction conditions for the duration of the run, which is usually long, since time is necessary for the hydrocarbons to oxidize sufficiently to give a mixture rich enough in oxidized products to warrant commercial recovery. This, of course, is unsatisfactory since most of the oxidized products are unstable and decompose at the reaction temperature to give rise to undesired products which complicate the problem of recovery or else result in a waste of valuable material. If the temperature of operation is maintained sufficiently low to prevent this decomposition, the process becomes unduly long because of the consequent lower reaction rate.

A series of catalysts, however, has been developed to speed up the reaction rate at temperatures sufficiently low to preclude any undue amount of decomposition. For these catalysts to be sufficiently effective to warrant their use they must be in intimate contact with the oil to be oxidized. For this reason most of the materials mentioned in the patent literature are of a soluble nature and consist principally of the organic salts of the metals comprising the fifth and sixth groups of the periodic system.[4] Such catalysts as are mentioned here have been claimed: [5] metal enolates as manganese acetyl acetone,[a] oleates or stearates of manganese, copper or iron,[b] stearate or cinnamate of barium, calcium, magnesium, aluminum,[c] resinates, oleates, enolates of the alkali metals, magnesium, aluminum, or manganese,[d] borates of cerium, cadmium, aluminum, iron, and zinc,[e] organic nitrogenous bases as hexamethylene-tetramine, aniline, pyridine, quinoline, etc., with inorganic catalysts,[f] nitrogen oxides,[g] etc. The use of such catalysts makes possible a working temperature of from 100° to 150° C. The use of pressure is frequently resorted to when low boiling hydrocarbon material is being oxidized. By having the liquid depth sufficient to allow practically all of the oxygen introduced at the bottom to be consumed before it reaches the vapor space above, the formation of explosive mixtures is prevented and all hazard removed from the operation.

Resort is occasionally had to the addition of alkaline material to the oil undergoing treatment to react with the acids formed and thus to remove

[3] For bibliography *see* Kelber, *Ber.* **53**, 66 (1920); Solway and Williams, *J. Chem. Soc.* **121**, 1343 (1922); Franck, *Chem. Ztg.* **44**, 309 (1920).
[4] For the preparation of metallic soaps *see* Whitmore and Lauro, *Ind. Eng. Chem.* **22**, 646-9 (1930).
[5] a. Brit. Pat. 303,268 (1927) I. G. Farbenind; b. Brit. Pat. 309,382 (1927) Alox Chem. Corpn.; c. Brit. Pat. 310,069 (1927) I. G. Farbenind; d. Brit. Pat. 312,388 (1928) I. G. Farbenind; e. Brit. Pat. 325,234 (1928) I. G. Farbenind; f. U.S. Pat. 1,762,688 (1929) Hofmann to I. G. Farbenind; Brit. Pat. 298,704 (1927) I. G. Farbenind; *compare* Brit. Pat. 284,616 and *Rubber Age* **20**, 27, 30 (1926) claiming use of basic organic nitrogen compounds as urea as antioxidants for oils; g. Brit. Pat. 324,492 (1928); Fr. Pat. 677,859 (1929) I. G. Farbenind.

them from the scene of reaction.[6] The acid is subsequently regenerated from the alkaline salts which form. This practice has also been claimed for aromatic hydrocarbon oxidation.[7]

Temperature control and heat economy may be obtained in such liquid phase processes by using the cool oil to be treated as a medium for removing the heat generated in the reaction vessel. For this purpose, the vessel is jacketed and the cool oil circulated through the annular space before passing it into the main body of hot oil.[8]

Based on the experience of the German Dye Trust, Krauch has made the statement that in the oxidation of the higher molecular weight paraffin hydrocarbons the oxygen does not attack the hydrocarbon molecules at the ends but rather near the middle to form large fragments.[9] Support is given to this view by the facts that the acids formed contain about half the number of carbon atoms of the starting hydrocarbons and that only small amounts of carbon dioxide and oxidation products of the lower hydrocarbons are formed. It is probable, however, that a certain amount of oxidation takes place at the ends of the hydrocarbon molecules, and that any higher alcohols thus formed react with the acids to give esters. In the vapor phase processes, where, in general, higher temperatures have been employed, this formation of such heavy molecules would largely be limited by the thermal stability, a condition not necessarily true of the liquid phase catalytic processes.

The majority of the work on the vapor phase oxidation mechanism of the hydrocarbons higher than butane has been for the purpose of studying the operation of gasoline internal combustion engines. As these studies have been largely devoted to anti-knock action a discussion may well be reserved for that section. However, some of the work is relevant.

Freund[10] has conducted a series of experiments on two gasolines, one from a paraffin base Galician crude, the other from cracked petroleum originating in the western part of this country. Vapors of these gasolines were passed over granulated petroleum coke heated to 400° to 500° C. in an iron tube so arranged that either air or nitrogen could be passed in simultaneously with the oil vapors. It was shown that thermal decomposition occurred at the same time that oxidation of the hydrocarbons took place. A confusion of products was formed. Mixtures containing carboxylic acids, esters, alcohols, phenols, olefins, aromatics, water and carbon dioxide were obtained. The oxidation could be made to predominate over the pyrogenic decomposition by use of increased proportions of air, longer times of contact, or higher temperatures. The evidence for hydrocarbon decomposition consists largely in the formation of the olefinic and aromatic hydrocarbons. Actually the reactions which probably occur must be very complex since even with single hydrocarbons of relatively low molecular

[6] U.S. Pat. 335,962 (1886) Schaal.
[7] a. Ger. Pat. 364,442 (1922) Fischer; b. Brit. Pat. 182,487 (1923) Eckert.
[8] Ger. Pat. 490,249 (1923) I. G. Farbenind.
[9] Krauch, *Proc. 2nd. Internal. Conf. Bit. Coal* 1928, 34-47, Carnegie Inst. Tech., Pittsburgh.
[10] Freund, *Z. angew. Chem.* 40, 368-74 (1927).

weight, considerable controversy still exists as to mechanism even after much experimental evidence has been accumulated.

The slow oxidation of a gaseous mixture containing 42 per cent hexane, 57 per cent oxygen, and 1 per cent nitrogen, at constant volume and temperature, at first proceeds with only a slight change in pressure although the actual reactions may proceed at a rapid rate during this stage. The pressure increases after this first stage. Surface retards the second step. The primary reaction is considered to be probably the formation of unstable intermediate compounds such as peroxides. Secondary reactions consist of the decomposition of these unstable oxidation intermediates into water, olefines, acids, carbon oxides, etc. These decomposition products, especially the unsaturated hydrocarbons, form further oxidation products by a process similar to the original reactions, and the final products may consist of simple aldehydes, carbon oxides and water if sufficient oxygen is originally present. If insufficient oxygen for complete combustion is present, the decomposition of the final peroxide compounds represents the last step in the process and probably accounts for the rise in pressure after the oxygen is consumed.[11] A similar mechanism has been observed with air-pentane mixtures.[12] As the temperature of such a mixture is gradually increased, no carbon dioxide or aldehydes are formed until a temperature within $10°$ C. of the explosion temperature is reached. At this point the pressure increase is rapid and considerable amounts of aldehydes and carbon dioxide appear.

The early hydroxylation theory of hydrocarbon oxidation has been applied to the higher hydrocarbons largely on the basis of composition of the products obtained, rather than by the isolation of the first steps of the process. Landa[13] subjected a white paraffin wax melting at $51°$ C. and boiling at $360°$ C. to slow combustion at $280°$ to $300°$ C. by passing a current of air through the liquid. No catalyst was used. Identified products consisted of formaldehyde, propaldehyde, butaldehyde, heptaldehyde, octaldehyde, and decaldehyde, together with acetone, methyl ethyl ketone, methanol and ethanol. The presence of these products was held to be a clear indication of the hydroxylation mechanism of the process. Results such as these are apt to be very misleading as a basis for mechanism studies, however, because of the many decomposition and side reactions possible.

Wheeler and Blair[14] also formulate a process based on the hydroxylation theory for the slow oxidation of hexane after having noted the formation of large quantities of aldehydes. Callendar[15] has also obtained formaldehyde and acetaldehyde as well as higher aldehydes in the oxidation of hexane.

[11] *See* Brunner, *Helv. Chim. Acta* 11, 881-97 (1928); Brunner and Rideal, *J. Chem. Soc.* **1928**, 1162-70, 2824-5.
[12] Dumanois and Mondain-Monval, *Compt. rend.* **189**, 761-3 (1929).
[13] Landa, *Compt. rend.* 186, 589-91 (1928).
[14] Wheeler and Blair, *J. Soc. Chem. Ind.* 42, 491T (1923).
[15] Callendar, *Aeron. Res. Com. (London) Reports and Memoranda* No. 1062, "Dopes and Detonation," 2nd Report.

Recently, Pope, Dykstra, and Edgar [16] have reported the results of their very careful work on the homogeneous vapor phase oxidation of n-octane. Practically theoretical mixtures of air and octane vapors were passed through tubes of Pyrex glass one inch in diameter and 36 inches long. Experiments were performed both at constant temperature and with slowly increased temperatures. Both liquid and gas analyses were made throughout the experimentation. No absorption of oxygen occurred below 200° C. Oxygen is regularly absorbed until 2 mols per mol of octane have disappeared in the temperature interval 200° to 270° C. Between 270° and 320° C., pulsations occur and oxygen consumption increases to 4½ mols. Up to 650° C., however, only 5½ mols have been consumed. Above 650° C., the reaction is rapid and oxygen consumption increases. The oxidation of heptaldehyde and butyraldehyde were also studied. A very simple mechanism was proposed on the basis of the results:

$$C_8H_{18} + O_2 = C_7H_{15}CHO + H_2O + \begin{cases} \xrightarrow{O_2} & C_6H_{13}CHO + 2H_2O + CO \\ \xrightarrow{1.5O_2} & C_6H_{13}CHO + 2H_2O + CO_2 \end{cases}$$
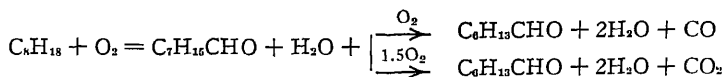
It is to be noted, however, that the reaction was decidedly luminous in certain temperature intervals above 270° C., and that up to 250° C., no carbon monoxide had formed and only small amounts of carbon dioxide notwithstanding that one mol of oxygen had been absorbed per mol of octane. The fact that carbon monoxide formation is suppressed by packing further suggests a chain type of reaction. Up to 250° C. the first step with formation of water is indicated.

In continuing their experimentation the same authors studied the oxidation of five isomeric octanes.[17] Although this work was not as complete as that on the n-octane, it does show some interesting relations. In general, the mechanism is the same as with n-octane. Oxygen first attacks the methyl group at the end of the longest free straight chain and oxidation then proceeds as before until a branch in the chain occurs at which point the oxidation is markedly suppressed.

While such results are of extreme interest and very valuable, they cover but a minute portion of the field of hydrocarbon oxidation and give no indication of what might occur in the presence of various catalytic agents. It would be interesting to have the results of experimental work, performed with equal care, on mixtures with restricted amounts of oxygen present and dealing with other hydrocarbons and in the presence of catalytic agents.

Recently, the vapor phase, low temperature, catalytic oxidation of the petroleum hydrocarbons has been developed. As early as 1905, Walther [18] patented such a process which was unsuccessful for several reasons, the most outstanding of which were the use of high ratios of air to hydro-

[16] Pope, Dykstra and Edgar, *J. Am. Chem. Soc.* 51, 1875-9 (1929).
[17] Pope, Dykstra and Edgar, *ibid.* 51, 2203-13 (1929).
[18] Brit. Pat. 21,941 (1905); Fr. Pat. 360,785; Ger. Pat. 168,291, Walther.

carbon and the use of excessively high temperatures. Less apparent reasons for the failure of the process may be found in the arrangement of the apparatus and in the choice of catalysts. As an example of the method used, a mineral oil distillate boiling above 300° C. was sprayed into a current of air mixed with steam and the mixture passed over copper oxide supported on asbestos and maintained at red heat. The process was auto-thermal and the catalyst maintained its temperature from the heat of the reaction. The products consisted of the lower fatty acids including acetic, solid aldehydes, organic acids solid at 0° C. and an oil 50 per cent of which distilled in the temperature range 140° to 300° C. Catalysts such as metallic oxides, peroxides or salts, i.e., iron oxides, lead oxide, cerium oxide, manganese peroxide, iron sulfate, calcium manganate, were recognized as carriers of oxygen and as promoters of the oxidation reaction.[19] The beneficial effect of steam as a diluent in controlling the reaction was not found essential to the process when such mild oxidation catalysts were used.

In studying the slow combustion of some of the higher hydrocarbons, Stepski[20] passed a stream of air saturated with the hydrocarbon vapors slowly over glowing platinum and then through a trap cooled to −15° C. Uncondensed fractions were brominated and the bromides separated by repeated fractional distillations at 15 mm. mercury pressure for analysis. Isopentane gave principally formaldehyde and ethylene along with other olefins, water, and carbon dioxide. The following equations were used to explain the slow oxidation of isopentane.

1. $\dfrac{CH_3}{CH_3}$>CH.CH$_2$.CH$_3$ + O $\longrightarrow$ $\dfrac{CH_3}{CH_3}$>CH.CH = CH$_2$ + H$_2$O
    $\qquad\qquad\qquad\qquad\qquad\qquad\dfrac{CH_2}{CH_3}$>C.CH$_2$.CH$_3$ + H$_2$O

2. $\dfrac{CH_3}{CH_3}$>CH.CH = CH$_2$ + O $\longrightarrow$ $\dfrac{CH_3}{CH_3}$>C = CH$_2$ + HCHO

    $\dfrac{CH_2}{CH_3}$>C.CH$_2$.CH$_3$ + O $\longrightarrow$ H$_2$CO + CH$_3$.CH = CH.CH$_3$
    $\qquad\qquad\qquad\qquad\qquad\qquad\longrightarrow$ H$_2$CO + CH$_2$ = CH.CH$_2$CH$_3$

3. $\dfrac{CH_3}{CH_3}$>C = CH$_2$ + O $\longrightarrow$ CH$_3$.CH = CH$_2$ + H$_2$CO

    CH$_3$.CH$_2$.CH = CH$_2$ + O $\longrightarrow$ CH$_3$.CH = CH$_2$ + H$_2$CO

4. CH$_3$.CH = CH$_2$ + O $\longrightarrow$ CH$_2$ = CH$_2$ + H$_2$CO.
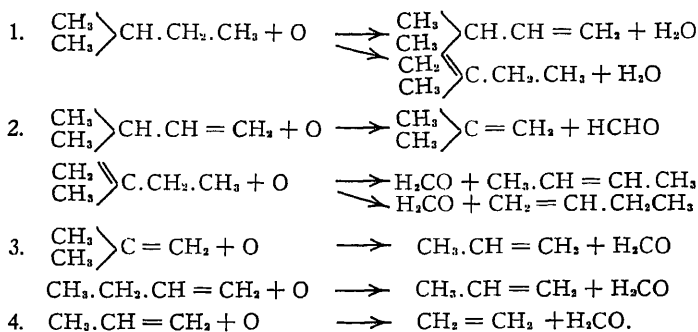
Similarly, n-hexane gave formaldehyde, ethylene, propylene, butylenes, amylenes, xylenes, water and carbon dioxide. The presence of butadiene in the products of these two oxidations is questionable.

The process of burning off hydrogen from a hydrocarbon to form a hydrocarbon of the same number of carbon atoms but less hydrogen in a manner similar to that outlined above is a more desirable process for producing olefins than straight thermal decomposition since by properly

[19] Ger. Pat. 227,178 (1909) Hausmann and Pilat.
[20] Stepski, *Monatsh.* 23, 773-801 (1902).

controlling the process it should be possible to form yields of olefins of the same number of carbon atoms. Also, by allowing the reaction to proceed further diolefins should result. As an example, the vapors of a petroleum oil fraction are passed through a heated zone such as a heating coil at a temperature of about 150° to 350° C. and at atmospheric pressure in the presence of from 5 to 20 cubic feet of air per pound of hydrocarbon.[21] The product has been dehydrogenated and is richer in olefins than the original oil. It may be useful in producing antiknock motor fuels by proper blending, as a flotation oil, as a paint and varnish vehicle, etc.

James [22] has claimed the formation of light hydrocarbons from heavy hydrocarbons by catalytically oxidizing the heavy oils in the vapor phase to form mixtures containing aldehydes, acids, alcohols, and ethers, and then subjecting this oxidized product to a second operation of thermal decomposition at temperatures above 450° C. and in the presence of nickel, copper, or iron. During this second operation the oxygen containing compounds decompose in such a way as to split out carbon dioxide, carbon monoxide, hydrogen, or water to leave lower molecular weight hydrocarbons. However, as the total liquid yield from the first or oxidation step is usually under 90 volume per cent and the total yield from the second or decomposition step is usually less than 90 volume per cent of the feed with less than 50 per cent of the final product boiling below 200° C., the motor fuel yields are not very high.

Notwithstanding the fact that the oxidation of hydrocarbons is an extremely favorable reaction thermodynamically, the rate at which paraffinic hydrocarbons are oxidized at temperatures sufficiently low to prevent excessive decomposition of the oxygenated products formed is very slow. Because of this inertness of the paraffinic hydrocarbons, processes have been devised which utilize a previous thermal decomposition to form certain proportions of olefinic hydrocarbons in the oils used. Subsequent oxidations may be obtained at lower temperatures and with less decomposition. Frank showed in 1920 [23] that when the hydrocarbon fragments formed by cracking were brought, in the nascent state, into contact with oxygen over certain catalysts, oxidation to fatty acids was rapid and complete. For instance, by heating paraffin at 150° C. for from 2 to 4 hours with a lead catalyst a product was obtained which had a saponification number of 250 to 350 and an acid number of 220 to 230. Over 18 per cent of the ethyl esters of the mixture obtained boiled up to 250° C. and 78 per cent consisted of the esters of acids higher than caproic. Esterification with glycol resulted in the formation of a clear yellow solid fat, edible and suitable for soap making. The catalyst was found to influence the character of the product. Thus, with a lead catalyst 30 per cent of low boiling fatty acids were obtained, whereas with vanadium the yield

[21] U.S. 1,767,363 (1930) Hopkins to Standard Oil Development Co.
[22] U.S. 1,597,796 (1926) James assr. to Byrnes; U.S. 1,597,798 (1926) James assr. to Byrnes.
[23] *Cf.* Hebler, *Erdöl. u. Ter.* 4, 333-4 (1928); *compare* Ellis, U.S. Pats. 1,516,720, 1,517,968 (1924).

was 57 per cent. Inorganic compounds of manganese, mercury, and chromium were also found to be effective. The addition of steam in such oxidation processes is made use of with the claim that better results are obtained. This is probably due to better heat dissipation and temperature control.[24]

To form both a distillate of lower boiling point as well as such oxidation products as acids, ketones, aldehydes, and alcohols, hydrocarbon oil is treated by a stepwise process.[25] The oil is first vaporized under pressure and passed over metallic oxide catalysts such as copper oxide or barium peroxide. The heavier of the evolved vapors are condensed and treated with air, oxygen, ozone, or nitrogen oxides and are then returned to the main stream of oil undergoing treatment. It is also possible to induce restricted oxidation by the use of metallic oxides capable of reduction at the temperature of the reaction. The process may be more readily controlled than when air or oxygen is used for the oxidation.

A series of reactions as follows may thus be carried out:

(1) Conversion of a paraffin into an olefin
$$C_nH_{2n+2} + O = C_nH_{2n} + H_2O$$

(2) Conversion of an olefin into a terpene
$$C_nH_{2n} + O_2 = C_nH_{2n-4} + 2H_2O$$

(3) Conversion of a terpene into an aromatic hydrocarbon
$$C_nH_{2n-4} = O = C_nH_{2n-6} + H_2O$$

(4) Conversion of a paraffin into an aromatic body
$$C_nH_{2n+2} + 4O = C_nH_{2n-6} + 4H_2O \quad \text{or}$$

(5) Conversion of an olefin into an aromatic body
$$C_nH_{2n} + 3O = C_nH_{2n-6} + 3H_2O$$

A mixture [26] consisting principally of olefins boiling in the range 110° to 300° C. is vaporized and passed through a malleable iron tube 40 inches long and 4 inches in diameter filled with iron oxide and heated electrically to 580° to 750° C., under just sufficient pressure to maintain the flow of vapors through the mass. A condensate amounting to 90 per cent of the oil treated is recovered, 47 per cent of which boils under 180° C. and when fractionated this portion of the condensate yields 7 per cent amylene and other hydrocarbons boiling under 40° C.; 8 per cent hexylene and other hydrocarbons boiling in the range 40° to 75°; 20 to 25 per cent benzene; olefins and other hydrocarbons boiling in the range 75° to 90° C.; 15 to 20 per cent toluene and olefins boiling 95° to 120°; 3 per cent distillate boiling 120° to 130° containing some octylene; 10 to 15 per cent distillate boiling 130° to 150° containing xylenes, olefins and some pinene; and 25 to 30 per cent distillate boiling 150° to 180°, of which about 18 per cent is limonene; the remainder being olefins and aromatic hydrocarbons. Practically no paraffin hydrocarbons are formed in the process. The ben-

[24] *See* U.S. Pat. 1,699,627 (1929) Palmer.
[25] U.S. Pat. 1,733,656 (1929) Egloff and Morrell.
[26] Brit. Pat. 106,080, Sept. 21, 1916; U.S. Pat. 1,224,787, May 1, 1917, Ramage, assr. to Bostaph Eng. Co.

zene and toluene may be freed from the olefins by the usual treatment with sulfuric acid and rectification. The Fe_2O_3 is successively reduced to Fe_3O_4, FeO and Fe, and the use of the contact mass is discontinued before the last stage of this reduction is completed. The ferric oxide may then be regenerated by blasting with steam and air without removing the material from the reaction tubes, or by blasting with steam alone with recovery of hydrogen as a by-product. Oxides of copper, cobalt, or nickel may be used instead of ferric oxide, but with copper oxides the reaction is not so readily controlled on account of the lower reduction temperature of the oxides. If reduction of the oxides is carried too far, cracking of the oil vapors takes place with formation of carbon. The reactions and proportions of different hydrocarbons in the product may be controlled to some extent by varying the temperature of the oxides in the tubes. The latter may be heated electrically if desired by nichrome wire set in alundum cement.

Experimental work has been in progress for several years on a process of liquid phase catalytic oxidation of hydrocarbon oils to produce motor fuels of high anti-knock and good blending properties.[27a] The process is conducted at temperatures of about 800° to 900° F., under pressures in the neighborhood of 20 atmospheres and in the presence of catalysts such as aluminum chloride, oxides of manganese, lead, iron, chromium, vanadium, zinc, copper, or lime. Although details of the operation of the process have not been publicized, some information regarding the nature of the oxygenated products is available.

For instance, Swann, Howard, and Reid [27b] passed air into petroleum hydrocarbons held in a still at about 750° F. (398.9° C.) under a pressure of 300 pounds per sq. in. (21.09 kgs. per sq. cm.) and analyzed the products contained in the aqueous layer. The apparatus used in the work consisted of a cylindrical steel still twenty-six feet high and four feet in diameter with a capacity of about 1000 gallons of oil. Heat exchangers were provided to preheat the feed and water coils were used to control the reflux. The vapor product passed through a condenser to a receiver. The gas oil used in the work was a Midcontinent distillate of 38.3° Bé density at 60° F. (15.6° C.). The oil had an initial boiling point of 552° F. (288.9° C.) and an 80 per cent over point of 701° F. (371.7° C.). A complete distillation curve for the oil up to 80 per cent is given.

The gas oil fed to the still was preheated to 500° F. (260° C.) and air at the rate of 400 cu. ft. (11.3 cb.m.) per min. was blown into the hot oil through the bottom of the still. Partial oxidation of the oil occurred and the heat of the reaction caused the temperature to rise to 750° F. (398.9° C.). The non-condensible gas produced had a composition of about 1.5 per cent carbon dioxide, no oxygen, 0.5 per cent combustibles, and the rest nitrogen. Besides the light product taken off through the

[27] a. Pennimann, Brit. Pat. 252,327 (1925); 255,020 (1925); 256,922 (1925); 257,886 (1925) and others; b. Swann, Howard and Reid, *Ind. Eng. Chem.* **23**, 1277-9 (1931).

vapor line, a certain amount of sludge was periodically withdrawn from the still bottom. The aqueous layer only was analyzed. Of thirty-seven barrels of gas oil used, sixteen barrels of oil and eight of aqueous product were recovered as distillate from the batch operation. The oil layer was water washed and the combined aqueous layer and the wash water were distilled into seven gallon cuts for storage and analysis.

The results of the analysis showed the following estimated yields of oxygenated organic compounds:

Product	Per Cent by Weight of Original Gas Oil
Acetaldehyde	0.55 (considerable lost)
Acetone ⎫ Methanol ⎪ Methyl acetate ⎬ Dimethyl acetal ⎭	1.9 (some lost)
Ethanol ⎫ Ethyl acetate, etc. ⎭	0.2
Allyl alcohol, etc.	0.35
Acetic acid	0.7

Data on the nature and yield of the hydrocarbon product are not available, although the process has been stated to have operated successfully on a semiplant scale with paraffin-base oils. That it has not yet been superlatively successful may be deduced from the lack of its widespread use. The possibility of sulfur removal from high sulfur crudes, such as the West Texas crudes, by such a process has probably been investigated but no authoritative information is available. It is probable that such an oxidation process will not greatly reduce the sulfur content in the product unless it is allowed to occur to an excessive extent.

In an attempt to prepare certain new chemical products by the vapor-phase, low temperature catalytic oxidation of the aliphatic hydrocarbons of petroleum, James [28] has developed a series of processes for control of the reactions, recovery of the products, and for utilization of the products.[29]

In James' experimental work it has been found that the oxides of certain metals of high atomic weight and low atomic volume, such as molybdenum and uranium, appear to be the most promising. With di-uranyl vanadate very good results were obtained. Good results have been obtained by passing the mixture of hydrocarbon vapor and air through a thin layer of uranium oxide and then on through two layers of catalyst consisting of the oxides of molybdenum. The uranium oxide is used in the first screen because this oxide has the specific property of catalyzing to a marked degree the aldehyde stage of oxidation, so that where acids are desired as the main product, this preliminary step brings about a higher yield of acids, the aldehydic bodies going over to acids in the second

[28] a. *Trans. Am. Inst. Chem. Eng.* 14, 189-199 (1921); b. *Chem. Met. Eng.* 26, 209-212 (1922).
[29] J. H. James, assr. to C. P. Byrnes, Trustee, patents as follows: U.S. Pats. 1,439,107 (1922), 1,549,316 (1925), 1,561,164 (1925), 1,588,836 (1926), 1,597,796 (1926), 1,597,797 (1926), 1,597,798 (1926), 1,667,419 (1928), 1,675,029 (1928), 1,681,185 (1928), 1,681,237 (1928), 1,681,238 (1928), 1,700,055 (1929), 1,700,056 (1929), 1,697,653 (1929), 1,721,958 (1929), 1,721,959 (1929), 1,759,620 (1930), 1,753,516 (1930); Brit. Pats. 138,113 (1919), 173,750 (1921), 174,099 (1920), 209,128 (1922), 259,293 (1925); Can. Pats. 210,808 (1921), 218,304 (1922), 231,473 (1923).

and third screens. Temperatures higher than 240° C. but not above 500° C. should be used for results of industrial value. In case high-molecular weight hydrocarbons are being treated, it is better to run a small amount of the heavy petroleum fraction—such as wax distillate, for example—with a large amount of a fraction of lower boiling range, such as gas, oil, or heavy kerosene, thereby effecting ready vaporization of the heavy portion and allowing a lower catalyst temperature for the reaction.

The products formed vary somewhat with the catalyst and the temperature employed, but in general represent all the stages of the oxidation of aliphatic hydrocarbons from alcohols to oxygenated acids, together with hydrocarbons and oxidized bodies resulting from secondary reactions. Alcohols, ketones, aldehydes, naphthenic acids and other substances formed make up a mixture of such complexity that quantitative analysis, even, is a hopelessly complicated task.[30]

One of the fields of application of this process is said to be the development of new fuel from the cheaper fractions of petroleum by carrying out the oxidation at higher temperatures. For example, with a fraction of Mexican fuel oil boiling from 300° to 360° C. and running the oxidation process by the three-screen method at 380° to 400° C. the liquid product obtained amounted to 80 per cent by volume of the oil treated. This product contained 30 per cent by volume of aldehydic fatty acids, 20 per cent by volume of other aldehydic bodies and the remaining 50 per cent consisted of other oxidized bodies and hydrocarbons. The latter were mostly of lower molecular weight than those of the original mixture, because of thermal decomposition of the oxygenated bodies. The distribution of the combined oxygen is shown by the analyses made on a product obtained by the oxidation of a "pressure still tar," the residue from the "cracking" stills of one of the pressure cracking processes:

Combined Oxygen in Fraction	Per Cent
Above 300° C.	4.10
Between 200° and 300° C.	6.48
Under 200° C.	12.32

The fraction under 300° C. is called "oxidized kerosene" by James, who suggests utilizing it as a fuel in internal combustion engines. Engine tests with a fuel made by the catalytic oxidation of kerosene and a similar fuel made by the oxidation of gas oil have been made [31] and the performance of the engine checked against other fuels. It was found that the oxidized kerosenes showed approximately the same power development as ordinary kerosene despite the fact that their thermal values are one-eighth less due to the oxygenated character. These oxidized kerosenes show lower detonation tendencies than the ordinary fuel and it is possible that with an engine specially designed for the fuel still better efficiencies would be obtainable with the new product. The explanation of the proper-

[30] *Compare* Burrell, *Ind. Eng. Chem.* 20, 602-8 (1928).
[31] James, *Trans. Am. Inst. Chem. Eng.* 14, 201-10 (1922).

ties of the kerosene when used as a motor fuel are not clear but might presumably be that since the original hydrocarbon molecules have been weakened toward oxidation because of their oxidized character, burning in the internal combustion engine is more complete with resultant higher efficiency.

The oxidation products obtained from the heavier fractions deserve attention from the standpoint of lubricant manufacture. The acid portion of the oxidation product has been found to sulfonate very readily. A promising application of the oxidation mixture in its entirety is in the field of ore flotation where it can serve primarily as a frothing oil in flotation mixtures replacing therein the expensive pine oil. Experimental evidence seems to point to the acid content of the oxidized mixture which gives this material its frothing character.

In the one-screen semi-industrial apparatus the excess heat developed was carried off by a system of cooling pipes, the closed ends of which were embedded in the catalyst. Either air or water could be used as the cooling medium. In this oxidation of aliphatic hydrocarbons the author usually prefers to keep the temperature of the catalyst below 400° C. (usually 280° to 380° C.) hence, in an apparatus larger than that used in the laboratory, the temperature tends to rise, because of the greater distance to any radiating surface and the non-conducting character of the catalyst and its carrier, which is usually asbestos.

In the cooling-tube system, one catalytic screen only was used, hence, all the air that was to be introduced had to be given to the reaction at one time. With more than one catalytic screen, the air is introduced in portions before entering each screen, being distributed among the screens usually in equal amounts. The triple-screen system also makes possible the use of different catalysts. It has been found that uranium oxide catalyzes the oxidation to the aldehyde stage, and at present uranium oxide is used for screen 1 and the molybdenum oxide mixture for screens 2 and 3. An example of the experimental result is shown: [28a]

CATALYSTS *: Three screens, all of molybdenum oxides, each 37.5 cm. in diameter and 1 cm. thick.

OIL USED: Pennsylvania petroleum; a product sold at one time during the war as fuel oil by one of the Pittsburgh refineries; it showed the following on distillation:

	Per Cent by Volume
First drop, 200° C.	
200°–250° C.	11
250°–300° C.	51
300°–350° C.	34
Residue above 350° C. and loss	4

Specific gravity of oil at 14.5° C. was 0.819. Olefin hydrocarbons (by the sulfuric acid test) was 7.5 per cent.

Time of run, 4 hours.

Average temperature of mixture leaving vaporizer, 310° C.

* Quoted by permission of the American Institute of Chemical Engineers.

Average temperature of first catalyst 335° C.

Average temperature of second catalyst 370° C.

Average temperature of third catalyst 370° C.

Volume of air at room temperature and pressure passing into vaporizer and on into first catalyst, 70 liters/minute.

Volume of air added at second catalyst, 30 liters/minute.

Volume of air added before entering third catalyst, 30 liters/minute.

For the second half of the run, "fume," gas (50 liters/minute) was taken from exit line and added as diluent to lower the temperature at screen number two.

Rate of oil feed to vaporizer, approximately 6 liters/hour.

Rate of water feed to vaporizer, approximately 6 liters/hour.

Vacuum on system at vaporizer, 5 cm. of mercury.

Gas Analysis	Per Cent by Volume
CO_2	2.9
O_2	2.9
C_nH_{2n}	2.5
CO	4.8
Undetermined (mostly N_2)	86.9

Volume of oil fed during run, 25.5 liters.

Volume of oily product (insoluble in water) recovered, 19.6 liters.

Specific gravity of product at 15.6° C. was 0.86.

The product had approximately the following composition:

	Per Cent
Aldehydic fatty acids	31
Aldehydes (above 200° C.)	20
Alcohols, volatile aldehydes and other oxidized bodies with hydrocarbons (by diff.)	49

The process can make use of any oil, even those very high in sulfur or cracked oils which are high in olefins. In fact, it has been noted that oils high in sulfur, like the Mexican oils, oxidize more readily.

One commercial plant [32] founded on the work of J. H. James has been built at Nyack, New York, to manufacture "Aldehol," a commercial alcohol denaturant. This plant having a capacity of 4,000 gallons of kerosene per day was so designed that heavier fractions such as gas oil or spindle oil could also be used for experimental purposes.

The apparatus is built with a series of catalyst screens with provision for feeding in fresh air between. In this way only sufficient air is admitted at each point to maintain the catalyst screens at the operating temperature of 350° to 410° C. The oil vapors, passing through all of the screens in succession, gradually becomes more and more fully oxidized. The operation is carried out under a 15 inch vacuum and the products collected in aluminum tubular condensers.

Besides forming "Aldehol" as a product the operation gives formaldehyde which is recovered from the water as hexamethylene-tetramine and certain soluble acids which have not been identified. The oxidized portion of the oil runs as high as 40 per cent of the total and consists principally of 30 to 40 per cent mixed aldehydes, 5 per cent free acids, 40 to 45 per cent alcohols, 10 per cent esters, and the rest ethers. About

[32] Bitler and James, *Trans. Am. Inst. Chem. Eng.* **20**, 95-100 (1927).

85 per cent total liquid recovery is realized, but with heavy oils the recovery may be as high as 92 per cent by volume. This plant apparently represents the first commercial scale oxidation of petroleum to be successfully operated, and opens up a wide field for the investigation of the effect of various factors such as catalyst, temperature, diluents on the operation.

Already, it has been shown that by oxidizing three cuts, naphtha, kerosene, and wax distillate, nitrocellulose solvents distilling through the whole range of "low boilers," "medium boilers," "high boilers," "plasticizers" and "softeners" may be prepared. These solvents are largely mixtures of esters, alcohols, and ethers with ketones and aldehydes removed.

Besides the extreme complexity of the mixture resulting from the vapor phase catalytic oxidation of various petroleum fractions, there are numerous other difficulties which act as hindrances to the commercial utilization of the products. This is especially true for the utilization of the acids that are formed. The acids are of the aldehydic or aldehydic-hydroxy type and are present in a mixture containing aldehydes of various molecular weights as well as unsaturated compounds. These compounds give a peculiar, objectionable odor to the acids and a brown or yellow color which is only intensified by polymerization and resinification when the acids are saponified with hot caustic solutions. The same difficulties have been encountered in the rather extensive researches being carried out, particularly in Germany, on the liquid phase, catalytic oxidation of hydrocarbon oils to form fatty acids.

Numerous methods have been proposed to overcome these hindrances to development and utilization of the processes. For separating the acids from the remainder of the oil and other oxidized bodies, lime has been added and the calcium soaps separated by filtration. Apparently, it is possible by this means to prevent the polymerization encountered when caustic is used and thus to insure a cleaner soap. The alkaline earth soap after being dried and comminuted is extracted with a solvent, such as gasoline, to remove any unsaponifiable matter. This purified soap may then be decomposed by the addition of sulfuric acid or by passing carbon dioxide into a solution of it to precipitate the calcium and free the organic acid. It is also possible to form the sodium soaps from these calcium compounds directly in a subsequent operation. Attempts have also been made to hydrogenate the aldehydes to alcohols and the olefins to paraffins in order to remove the difficulty caused by resinification and consequent deepening of color. By further oxidizing the aldehydic acids, dibasic acids may be formed and thus some of the inherent objectionable features removed from this product. This subsequent oxidation process may in some cases consist in treatment with such oxidizing agents as chromic acid, potassium permanganate, hydrogen peroxide, etc., for the purpose of bleaching the acid by the oxidation of resinous matter and color bodies.

By sulfonating the oxidized product obtained from a straight distillate

of Pennsylvania crude of 38° Bé, which has been subjected to the James process of catalytic oxidation, a valuable "activator" for insecticides has· been developed.[33] This sulfonated product is a clear maroon-colored liquid containing about 40 per cent oxygen and about 1.5 per cent sulfur, miscible with water in the form of an opalescent emulsion, and capable of "activating" nicotine sulfate solutions to such an extent that concentrations of nicotine of 1 to 4000 are effective insecticides.

Another process patent[34] describes the oxidation of liquid hydrocarbons by spraying through atomizers into cylinders heated to 80° C. and packed with pumice impregnated with nickel oxide. Air or air diluted with nitrogen is pumped into the bottom of these cylinders. The gaseous reaction product leaves the upper end of the cylinder and after passing through scrubber-condensers is returned to the cylinder where it meets fresh oxygen, while liquid reaction products pass out at the bottom into atomizers and are then likewise returned for further ·oxidation. The process is thus one of oxidation in stages by a process of recirculating the partial oxidation products.

For the purpose of producing efficient mineral-frothing agents from petroleum oil, the oil is oxidized in vapor phase in the presence of ultraviolet light.[35] In this process the oil is suitably atomized in a spray device and is mixed with the desired amount of air. This finely divided mist of oil in air is then passed over an enclosed ultra-violet lamp which presumably acts as a means of heating the mixture and to induce the oxidation reaction. The products are variable in composition depending upon operating conditions but are found to be most suitable when consisting largely of aldehydes or aldehyde-like bodies.

It is to be noted that in vapor phase processes such as those described by James the acids produced are aldehydic in nature and may depend upon this aldehydic character for utilization in the form of condensed products such as low grade resins, etc. Attempts to recover these acids in the form of sodium soaps usually leads to the formation of resins due to the resinifying action of the caustic. On the other hand, the numerous claims for the liquid phase oxidation process usually mention the formation of simple carboxylic acids or hydroxy-carboxylic acids which may be used to form edible fats by esterification with glycerol. This seems to indicate the somewhat milder oxidation possible in the liquid phase process.

The oxidation of hydrocarbons even to form oxygenated products rather than complete combustion products is a highly exothermic reaction and large quantities of heat must be removed per unit of oil treated. With laboratory scale apparatus this is not difficult to affect since the radiating surface of the reaction chamber is usually large in relation to the amount of material treated per unit of time and the heat of reaction may be effec-

[33] Inman, *Ind. Eng. Chem.* 21, 542-3 (1929).
[34] Brit. Pat. 148,892 (1920) Deutsche Erdol A.G.
[35] U.S. Pat. 1,678,403 (1928) Martin assr. to Minerals Separation North American Corpn.

tively radiated to the surroundings. In fact, most of the laboratory experiments have had to resort to the use of external sources of heating since the heat losses were larger than the heat generated.

However, as is usually the case, what is true of laboratory scale experiments is not true of commercial operation. Industrially it is necessary that large quantities of material be treated in relatively short periods of time in order for the process to be profitable. For this reason, it is necessary to employ either larger reaction chambers or a larger number of small reaction chambers in close proximity. In the one case heat transfer to the radiating surface is materially decreased and in the other effective radiation from the surface of the reaction tubes is prevented. Thus a difficulty of the first order has presented itself in the industrialization of these vapor phase oxidation processes. In the case of the liquid phase processes the mass of material at the reaction point has a large heat capacity and sudden and non-uniform changes in temperature are prevented. Heat conduction to the surface of the reaction chamber is better, evaporation may be relied upon to remove most of the heat of reaction, and a certain amount of cooling is obtained by the loss of heat necessary to bring the relatively cold oxidizing gas up to reaction temperature. Several methods present themselves for temperature control and heat removal.

By using low concentrations of air or oxygen with the oil vapors the extent of reaction may be limited to any desired amount. This acts very effectively in controlling the heat evolved during the reaction, since by properly controlling the temperature of the feed vapors the temperature of reaction may be prevented from rising to a point where complete oxidation would be induced and a larger amount of heat liberated. The excess oil vapor acts as a diluent to absorb the heat evolved by increasing slightly in temperature. However, unless auxiliary means are available for the removal of a portion of the heat only very low oxygen concentrations may be used if excessive temperatures are to be avoided as will be shown in a later chapter. Even with low oxygen concentrations and auxiliary heat removal by radiation the amount of oxidized material formed per pass is very small and unless recycling operations are possible, too low for commercial utilization.

A more satisfactory method is the addition of an inert gas or vapor to the reacting oil vapor-oxygen mixture. Thus, nitrogen, carbon dioxide or steam may be used. When the gases are used recovery of oxygenated products and unreacted oil depends upon the non-condensation of the diluent when the reaction gases are cooled. It is, however, necessary to use large volumes of the diluent gas in some instances and unless the products have a low vapor pressure considerable quantities will be lost in the gas or decomposed if the gas is recycled. Steam, however, is free from these objections and indeed serves as a scrubbing medium for the collection of products which are soluble in water. It is also useful in bringing the

oil vapors into the reaction zone when a heavy oil is to be treated by a process of steam distillation.[36]

This use of diluents is especially valuable when reaction tubes of large cross section are used. With small tubes which are used in bundles of several, a somewhat different method of temperature control is available. The tubes may be immersed in a bath of a liquid which boils at or near the reaction temperature. In a manner analogous to the liquid phase process the heat of reaction is used to vaporize liquid from this bath. These vapors may be externally condensed and the liquid returned. In this way the heat of reaction may be removed externally at any desired temperature. The details of this method of operation will be presented in a later part of the book.[37]

The use of ozone in the oxidation of the heavier hydrocarbons is subjected to the same restrictions surrounding its industrial use as with the natural gas hydrocarbons, chiefly cost. Consequently, even less work has been done with it in regard to the heavy hydrocarbons than is true of methane. Where ozonized air is passed into boiling n-hexane a series of oxidation products results consisting of aldehydes (formaldehyde, acetaldehyde in preponderance and higher aldehydes up to hexoic), fatty acids probably also up to six carbon atoms, and a mixture of esters.[38]

Examples have been given for the formation of ketones, acids, and other oxygen containing compounds by the treatment of aliphatic or hydroaromatic hydrocarbons such as are present in pressure distillate with carbon monoxide under pressure and in the presence of the anhydrous halides of aluminum or boron or both.[39] Such a process, advocated also for the oxidation of chlorinated or alkylated aromatics,[40] is of doubtful utility.

The hydration of cracked gasolines containing considerable quantities of olefins to form alcohols presents certain interesting phases, since the presence of higher alcohols in such gasolines would make possible the addition of methanol to form highly anti-knock motor fuels. On the basis of the fact that higher olefins do not yield alcohols when hydrated by absorption in sulfuric acid followed by dilution and distillation, it may be concluded that such a process would not be favorable. Even though the hydration reaction is thermodynamically possible, the actual realization would be involved with such difficulties as the use of high pressures, large amounts of steam, catalyst poisoning, polymerization, etc. No experimental data are available for such processes and no further conclusions may be drawn.

[36] For vapor pressure data *see* Cox, *Ind. Eng. Chem.* 15, 592 (1923); Calingaert and Davis, *ibid.* 17, 1287 (1925); Francis and Wood, *J. Chem. Soc.* 1926, 1420; Wilson, *Ind. Eng. Chem.* 20, 1363-6 (1928); Coats and Brown, *Univ. Mich. Dept. Eng. Research Cir.* No. 2 (1928).
[37] *See* some of the patents to Ellis in regard to temperature control for oil oxidation. U.S. Pat. 1,697,262, 3, 4, 5, 6, 7 (1929) Ellis to Ellis-Foster Co.
[38] a. Ledbury and Blair, *Div. Sci. Ind. Research, Special Report* No. 1; b. Blair, Wheeler, and Ledbury, *J. Soc. Chem. Ind.* 43, 287T (1924).
[39] Brit. Pat. 310,438 (1928) I. G. Farbenind.
[40] Dieterle and Eschenbach, *Arch. Pharm.* 265, 187-95 (1927); Brit. Pat. 3152 (1915) Longman; Fr. Pat. 664,611 (1928) I. G. Farbenind.

Chapter IX

Production of Hydrogen from Methane

Since the advent of the synthetic ammonia, synthetic methanol, and the hydrogenation of coal and oil processes, the demand for enormous quantities of cheap hydrogen has been insistent, and is at the present time constantly increasing. Hydrogen is now most generally being produced by the water-gas catalytic process from cheap coal and lignite. However, the high hydrogen content of the low molecular weight hydrocarbons as methane and ethane and the enormous quantities of them available principally as natural and refinery gas at a very low price, makes them potential sources of hydrogen that demand considerable attention. The successful production of hydrogen and carbon monoxide from methane especially is of great industrial and economic importance.

For this conversion of hydrocarbons into hydrogen three general processes have been considered:

(a) Complete or incomplete thermal decomposition. This process has been embodied in the Thermatomic Carbon Process in which methane is decomposed at temperatures of 1100° to 1200° C., according to the reaction, $CH_4 = C + 2H_2$.

(b) Partial oxidation with air or oxygen. Although considerable work has been done on partial oxidation with oxygen, it has had as its object either the formation of oxygenated compounds or the study of the mechanism of combustion. Very little work has been done with the direct object of producing hydrogen and carbon monoxide.

(c) Oxidation with steam. Although this process is endothermic and proceeds only at high temperatures, the advantages have made it important industrially and it is being used as a source of hydrogen especially in locations where methane is available at very low cost.

Combinations of both oxidation and decomposition processes may also be used. It is possible to form hydrogen from paraffinic hydrocarbons by a process of combined partial thermal decomposition and partial oxidation.

The Thermatomic process for the cracking of methane, or other gaseous hydrocarbons, makes use of brick checkerwork contained in furnaces fourteen feet in diameter and twenty-five feet high, and heated by the combustion of the same or similar gases as those being decomposed. In operation, the checkerwork is heated to about 1400° C. by the burning gas, combustion is stopped, and the gas to be cracked passed in until the tem-

perature has dropped to about 900° C. The operation is then repeated. By thus cracking a gas comprising 0.4 per cent by volume of carbon dioxide, 0.7 per cent olefins, 93.8 per cent methane, and 5.1 per cent nitrogen a resultant gas mixture comprising 0.9 per cent carbon dioxide, 1.3 per cent olefins, 85.4 per cent hydrogen, 1.1 per cent carbon monoxide, 5.0 per cent methane, and 6.3 per cent nitrogen is obtained.[1]

Only such processes as involve oxidation will be considered here. These processes result in the formation of hydrogen and carbon monoxide directly or hydrogen and carbon dioxide indirectly through the water-gas equilibrium.

THE OXIDATION OF METHANE WITH OXYGEN

The oxidation of methane has already been discussed from the viewpoint of forming valuable oxygenated products,* and a general consideration of the mechanism involved need not be repeated. However, a consideration of some of the experimental results which are particularly relevant and of the thermodynamics involved in the production of hydrogen according to the equation:

$$2CH_4 + O_2 (+ 3.8N_2) = 2CO + 4H_2 (+ 3.8N_2) \tag{1}$$
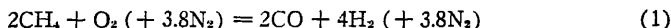
will make possible a clearer conception of the difficulties to be surmounted.

Bone and Townend [2] in investigating the rate of combustion of various gases, burned a mixture of the composition, $2CH_4 + O_2$, at 350° C. and at constant volume with the expectation of forming hydrogen and carbon monoxide by reaction (1). A condensation of water was obtained, however, and the gaseous products consisted largely of unreacted methane and carbon dioxide, showing that reaction had probably occurred according to the equation:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \tag{2}$$

No free hydrogen was formed. No general conclusions may be drawn from this work as the experiments were all at constant volume and covered but a narrow temperature range.

When, however, an equimolar mixture of (a) ethane and oxygen was exploded by an electric spark a black cloud of carbon resulted apparently showing that the hydrogen had been preferentially attacked. With mixtures of (b) 1 mol acetylene, 2 mols hydrogen, 1 mol oxygen and (c) 1 mol ethylene, 1 mol hydrogen, 1 mol oxygen, mixtures having the same ratio of carbon and hydrogen to oxygen as the ethane-oxygen mixture, the explosions did not give any carbon deposit and very little water. In these latter explosions the hydrocarbon apparently burned to carbon dioxide

[1] a. Moore, Buffalo Meeting, Pet. Div., Am. Chem. Soc., Sept. 1931; b. Rosenstein, *Chem. Met. Eng.* **38**, 636 (1931), discusses the formation of hydrogen by this method for use in ammonia synthesis by the Shell Chemical Co. *Compare also* Odell, *U. S. Bur. Mines Tech. Paper* No. 483 (1930), and Tyrer, Brit. Pat. 340,050 (3.10.29) Imperial Chemical Industries, Ltd.
* *See* Chapter VI.
[2] Bone and Townend, "Flame and Combustion in Gases," London, Longmans, Green & Co., Ltd., 1927, p. 361.

and hydrogen and the hydrogen originally present was left untouched.[3] Also, when mixtures of (d) 1 mol methane, 1 mol oxygen and x mols hydrogen were exploded, no carbon was deposited and the methane apparently burned preferentially.[4]

From these experiments of Bone, from those of Henry mentioned in Chapter VI, and from those of Landolt,[5] it has been concluded that hydrogen has been found to burn before methane at low temperatures in contact with platinum catalysts, and even at relatively high temperatures in platinum tubes;[5] and that methane burns before hydrogen when exploded or when kept in borosilicate bulbs at moderate temperatures.

An analysis of the conditions and results of experiments with mixtures (a), (b) and (c) (Bone), which were designed to show that the theory of partial decomposition was untenable, however, discloses that the free energy content of the mixtures was not the same, that of (a) being the lowest. The result is that flame temperature could be much higher in the case of (b) and (c) with the result that the reaction

$$H_2O + C = CO + H_2$$
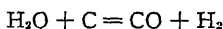
could occur and thus give a semblance to preferential combustion of the carbon. The results and conclusions from the competitive oxidation experiments of mixture (d), which attempt to show that methane is burned preferentially to hydrogen, are equally misleading. Thus, Coward and Dixon [6] have shown the instantaneous ignition temperatures in air of hydrogen, carbon monoxide and methane to be 631°, 696°, and 725° C., respectively, and White [7] gives the following ignition points with copper oxide: hydrogen, 175° to 180° C.; carbon monoxide, 100° to 105° C.; methane, above 455° C. It is thus probable that hydrogen would first burn to give water and generate sufficient heat to raise the temperature to a point where the methane reforming reaction

$$CH_4 + H_2O = CO + 3H_2 \tag{4}$$

would occur. The results of such a step-wise process would give results closely resembling those of Bone. Oxygen would be distributed between carbon and hydrogen very nearly in proportion to the requirements of equilibrium at the temperatures and pressures obtained.

In their extensive investigations on the combustion of methane and higher hydrocarbons, Wheeler and Blair [8] covered a wide range of experimental conditions and obtained results, some of which are of interest in the present case. The earlier experiments were not conducted in the presence of catalysts, however, but in the later work surfaces such as porcelain and pumice and catalysts such as the metallic oxides were used.

[3] Bone, *Proc. Roy. Inst.* 19, 82 (1908).
[4] Bone, *Phil. Trans.* 215, 298 (1915).
[5] *Pogg. Ann.* 99, 411 (1856).
[6] Coward and Dixon, reference in Bone and Townend, "Flames and Combustion in Gases," *loc. cit.*, p. 66.
[7] White, "Gas and Fuel Analysis." New York, McGraw-Hill Book Co., 1913, p. 54.
[8] *J. Soc. Chem. Ind.* 41, 303T (1922); 42, 81T, 260T, 491T (1923).

Some of their results from recirculation experiments shown in Table XV and their conclusions should be considered.

TABLE XV.—*Oxidation of Methane.*[9]

Recirculation experiments—iron oxide catalyst.
At temperatures below 700° C. with mixtures containing from 6.3 to 40.3 per cent oxygen, no hydrogen appeared in the product.

Temp.	—Initial Gas—		CO$_2$	O$_2$	CO	CH$_4$	H$_2$
° C.	CH$_4$	O$_2$					
700	55.5	44.5	0.6	30.7	13.6	50.6	4.5
720	50.6	49.4	6.1	4.7	48.5	34.0	6.7
740	54.3	45.7	7.3	1.9	39.9	34.9	16.0

The increased yields of carbon monoxide and hydrogen which were obtained at the higher temperatures were attributed to the fact that decomposition and oxidation of intermediate products are accelerated more by the catalyst at low temperatures than is the oxidation of the hydrocarbon, whereas at higher temperatures the rate of oxidation increases so that hydrogen and carbon monoxide tend to accumulate in the gaseous mixture.

From results obtained with metallic and metallic oxide catalysts they conclude, that metallic catalysts do not accelerate the oxidation of hydrogen and carbon monoxide so exclusively as do the metallic oxide catalysts. With a metal catalyst, all the gases present have to react with a temporary intermediate oxide. On the other hand, hydrogen and carbon monoxide can directly reduce the oxide catalysts even at low temperatures, while the hydrocarbons cannot. For this reason hydrogen and carbon monoxide are more readily formed with a metallic catalyst than with a metallic oxide catalyst. It is evident that they do not consider equilibrium relationships of any importance since the composition of products is explained on the basis of relative reaction rates. Although this attitude may be well taken on the basis of the results, the fact that methane is very unreactive and requires an active catalyst for oxidation at low temperatures to form intermediates does not seem to have been recognized.

Non-catalytic combustions conducted at still higher temperatures of about 1000° C. have resulted in the formation of considerable carbon monoxide, very little formaldehyde, and small amounts of carbon dioxide. Barl decomposed 36.5 per cent of the methane in a methane-air mixture to obtain 32.5 per cent carbon monoxide, 1.8 per cent formaldehyde, and 2.2 per cent of carbon dioxide [10] at a reported temperature of 1000° C. The fact that some formaldehyde was able to withstand decomposition at this temperature indicates that either its time of contact with this high temperature was exceedingly short or that its rate of decomposition is slow even at 1000° C. The former seems to be nearer the truth since the two oxides of carbon are not present in the ratio demanded by the equilibrium for this temperature. Consideration of the experimental results of Rhead

[9] Wheeler and Blair. *J. Soc. Chem. Ind.* **42**, 84T (1923).
[10] Barl, *Z. angew. Chem.* **36**, 297 (1923).

and Wheeler [11] shows that the ratio more nearly corresponds to a temperature slightly lower than 850° C., which leads to the conclusion that the effective temperature in this case was not 1000° C. as reported but more nearly 800° to 850° C. The later work of Tropsch [12] yielded comparable results. At 1000° C. he was able to obtain considerable yields of carbon monoxide and slight amounts of formaldehyde.

While attempting to produce oxygenated derivatives by the catalytic oxidation of methane, Layng and Soukup [13] obtained some interesting results by the use of nitrogen dioxide as a catalyst. The best results of their reported experiments from the standpoint of hydrogen and carbon monoxide production are given in Table XVI.

TABLE XVI.—*Oxidation of Methane in Presence of NO_2.*
Temperature 635° C., catalyst 0.35 per cent NO_2 by volume of inlet gas. Time of contact 1.81 seconds.

Gas	Inlet Gas Composition	Exit Gas Composition
CO_2	0.2	5.1 *
Olefins	—	—
O_2	48.0	5.5
H_2	0	7.8
CO	0.2	39.3
C_2H_6	10.9	2.6
CH_4	34.0	25.3
N_2	6.7	14.4

* Includes any gaseous catalysts which remained in effluent gas after scrubbing and was, therefore, removed as "CO_2" in KOH absorption pipet.

These results are to be contrasted with those obtained with solid catalysts such as copper, copper oxide, silver oxide, barium peroxide, platinum oxide, and active charcoal in which only very small amounts of hydrogen and carbon monoxide were obtained. From the fact that rather high yields of oxygenated compounds could also be obtained with the gaseous catalyst, it would seem that decomposition of these compounds played an important part in the production of the hydrogen and carbon monoxide.

Another instance of the use of gaseous catalysts is to be found in the work of Medvedev.[14] In these experiments small amounts of hydrochloric acid were used in the methane-oxygen mixture and catalysts composed of a mixture of the phosphates of tin, iron, and aluminum used in addition. Excellent results are reported from runs made in a series of tubes with recirculation of the gas at a temperature of 600° C. Ninety per cent of the original methane was decomposed to produce 15 per cent of formaldehyde with the other products largely carbon monoxide and hydrogen. Formaldehyde is probably first formed and then broken down to hydrogen and carbon monoxide. The mechanism of the action of the hydrochloric acid gas in this case is somewhat obscure but might be through the formation of intermediate chlorinated derivatives which are later oxidized.

[11] Rhead and Wheeler, *J. Chem. Soc.* **97**, 2178 (1910).
[12] Tropsch, *Brennstoff. Chem.* **5**, 37 (1924).
[13] Layng and Soukup, *Ind. Eng. Chem.* **20**, 1052 (1928).
[14] Medvedev, *Trans. Karpov Inst. Chem.* **3**, 54 (1924); **4**, 117 (1925).

In studying the combustion of gases under pressure for the purpose of producing carbon, Francis [15] made a number of experiments in which mixtures of methane and oxygen were exploded under pressure. In some cases analyses were made of the gases resulting from the combustion. For instance, a mixture of 69 per cent methane in oxygen was exploded from an initial pressure of 14 atmospheres to yield a dry gas composed of methane 45 per cent, hydrogen 35.7 per cent, carbon monoxide 15.9 per cent and carbon dioxide 3.3 per cent. A deposit of carbon amounting to 12.6 per cent based on a carbon balance was also obtained. This result parallels that obtained in one of the many pressure combustion experiments made by Townend.[16] The results of this type of combustion are of interest here only in showing the trend of some of the experimental work in a study of combustion mechanism.

A calculation of the equilibrium constants for reactions (1) and (2) may be made from available thermodynamic data.[17] These calculations give for the reaction:
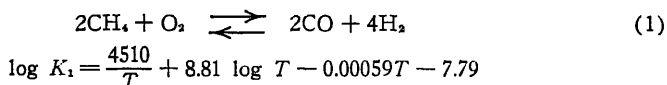
$$2CH_4 + O_2 \;\rightleftarrows\; 2CO + 4H_2 \tag{1}$$

$$\log K_1 = \frac{4510}{T} + 8.81 \log T - 0.00059T - 7.79$$

Where

$$K_1 = \frac{p^2{}_{CO} \times p^4{}_{H_2}}{p^2{}_{CH_4} \times p{}_{O_2}}$$

and for the reaction:

$$CH_4 + 2O_2 \;\rightleftarrows\; CO_2 + 2H_2O \tag{2}$$

$$\log K_2 = \frac{42{,}151}{T} + 2.075 \log T - 0.000405T + 0.000000094T^2 - 6.58$$
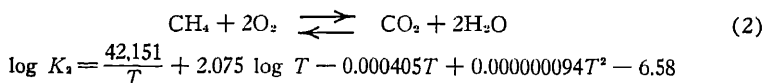
Where

$$K_2 = \frac{p{}_{CO_2} \times p^2{}_{H_2O}}{p{}_{CH_4} \times p^2{}_{O_2}}.$$

A comparison of these two equations shows that the equilibria do not become of the same value until very high temperatures are reached. Since this is true, mixtures containing only sufficient oxygen for reaction (1) will react according to equation (2) to the extent of using up most of the oxygen in the reaction at relatively low temperatures. This would leave unreacted methane which would be in equilibrium with carbon dioxide and water according to the equations:

$$CH_4 + CO_2 \;\rightleftarrows\; 2CO + 2H_2, \tag{3}$$

and

$$CH_4 + H_2O \;\rightleftarrows\; CO + 3H_2, \tag{4}$$

or

$$CH_4 + 2H_2O \;\rightleftarrows\; CO_2 + 4H_2, \tag{5}$$
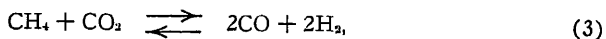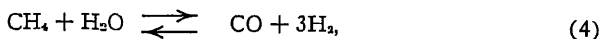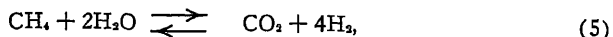
[15] Francis, Thesis, Worcester Polytechnic Institute, 1929: Am. Chem. Soc. (1931), Indianapolis, Ind.

[16] Townend, *Proc. Roy. Soc.* 116A, 637-63 (1927).

[17] Lewis and Randall, "Thermodynamics and Free Energy of Chemical Substances," New York, McGraw-Hill Book Co., Inc., 1923.

through the catalytic water-gas reaction:

$$H_2O + CO \rightleftharpoons CO_2 + H_2. \tag{6}$$
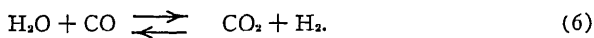
With short times of contact, i.e., with rapid rates of gas flow through the heated zone it is also possible that the time will not be sufficient for equilibrium to be established in the reacting mixture of gases and that hydrogen and carbon monoxide will form from the decomposition of intermediately formed formaldehyde as:

$$CH_4 + O_2 \rightleftharpoons H_2CO + H_2O \rightleftharpoons H_2 + CO + H_2O \tag{7}$$
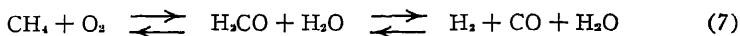
Also, reactions (3) and (4) do not occur to any great extent to the right, as written, until high temperatures are reached, as will be shown later, and also require active catalysts; reaction (6) does not occur very rapidly, requiring an active catalyst. As a result any hydrogen and carbon monoxide that may be formed from low temperature combustion of methane with a deficiency of oxygen very probably represents the decomposition products of intermediate oxygenated compounds.

In attempting to check the theoretical calculations for reaction of methane with oxygen to form hydrogen and carbon monoxide, Liander [18a] passed mixtures of methane and air, with the proportion of methane to oxygen of $2:1$ through reaction tubes at various temperatures both with and without catalysts present. He found that with no catalyst present the reaction occurred in such a way as to produce water and carbon dioxide at temperatures of 700° to 850° C. With catalysts, such as supported nickel, present the water formed in the primary reaction presumably reacted with the methane remaining to give hydrogen and carbon monoxide. Without a catalyst this latter reaction is so slow that the water formed condenses on the cooler parts of the apparatus and is thus removed from the reaction zone long before appreciable reaction occurs.

Although involved principally with the formation of acetylene from methane, the experiments of Fischer and Pichler [18b] on the high temperature, partial combustion of methane are of interest from the standpoint of hydrogen and carbon monoxide formation by this method since they. throw light on some of the complications that are to be expected in the way of side reactions. Mixtures of air and methane were passed through small tubes at temperatures of 1000° to 1400° C. and with a time of contact of about 0.005 seconds. The methane was more or less completely converted to acetylene, hydrogen, and carbon monoxide. Under similar conditions but at a higher pressure of 120 atmospheres at the start, little or no acetylene resulted and the methane was more or less completely converted to carbon, carbon monoxide, and hydrogen. Coke oven gas containing about 23 per cent methane could be practically completely converted to hydrogen and carbon monoxide at 1200° C. by passing it in

[18] a. *Trans. Faraday Soc.* **25**, 462-72 (1929). b. Fischer and Pichler, *Brennstoff Chem.* **11**, 501-7 (1930).

admixture with air or oxygen through a tube which was packed with broken pottery. The use of higher oxygen ratios and longer times of contact at these temperatures would probably lead to the complete destruction of the acetylene. Nevertheless, the results are indicative of the nature of some of the side reactions to be expected.

A number of other side reactions also occur at the same time and complicate any analysis of the reactions involved. Deposition of carbon has been attributed to the decomposition of methane according to:

$$CH_4 = C + 2H_2$$
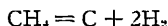
on the basis of the findings of Mayer and his collaborators[19] that this reaction sets in at about 250° C. and is almost complete at 850° C. This assumption does not seem in accord with present free energy data which indicates that methane is stable to its elements up to about 575° C.,[17] and the fact that methane when heated to 1300° C. is not completely decomposed at the end of an hour according to this reaction. Between temperatures of 1000° to 1200° C., comparatively long heating periods are required even in the presence of such active catalysts as iron and nickel to decompose methane into carbon and hydrogen.[20] Such catalysts as porcelain, silica, etc., are much less active toward this decomposition. The rate of decomposition of methane is inappreciable below 700° C. unless a large surface of porous material is exposed.[21]

Another reaction may also interfere by causing deposition of carbon in the reaction zone:

$$2CO \rightleftharpoons C + CO_2$$
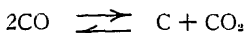
The reverse of this reaction, the reduction of carbon dioxide by carbon to form carbon monoxide is of considerable industrial importance being involved in the manufacture of producer gas, etc., and has been carefully studied. The free energy change of this reaction is such that the equilibrium constant becomes equal to 1 at a temperature of about 1000° K (727° C.). Thus for the reaction:

$$C + CO_2 \rightleftharpoons 2CO$$
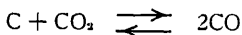
$$\Delta F = 40910 - 4.9T\ln T + 0.00495T^2 - 0.00000051T^3 - 12.66T.$$

As the temperature increases from this value the reduction of carbon dioxide proceeds strongly. The rate of reduction is measurably fast, being about twice as rapid as the reaction between water and carbon, $2H_2O + C = CO_2 + 2H_2$, at this temperature. At temperatures somewhat lower than this, however, the rate of carbon deposition from carbon monoxide gas is not very rapid.

[19] *J. Gasbeleucht.* **52**, 166, etc. (1909).
[20] Stanley and Nash, *J. Soc. Chem. Ind.* **48**, 1T (1929).
[21] Bone and Coward, *J. Chem. Soc.* **93**, 1197 (1908).

At temperatures up to 500° or 600° C. the reaction to form formaldehyde:

$$CH_4 + O_2 = CH_2O + H_2O$$
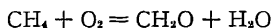
would give misleading results particularly if the times of contact were so short as to prevent the complete decomposition of formaldehyde to hydrogen and carbon monoxide or its secondary oxidation.

Another reaction of some importance which may further complicate the results is that of methane with carbon dioxide as:

$$CH_4 + CO_2 = 2CO + 2H_2. \tag{3}$$

which occurs with a free energy change represented by:

$$\Delta F_3 = 56,950 - 15.08T \ln T + 0.01078T^2 - 0.00000031T^3 + 30.34T.$$

$$- \log K_3 = + \frac{12450}{T} - 7.59 \log T + 0.002367 - 0.000000068T^2 + 6.64$$

where:

$$K_3 = \frac{p^2{}_{CO} \times p^2{}_{H_2}}{p_{CH_4} \times p_{CO_2}}.$$

The equilibrium constant for this reaction is only 3.55×10^{-6} at 400° C. but increases with temperature so that at 500° C. it becomes 0.00178, showing that if the reaction rate is sufficiently high some interaction of methane and carbon dioxide may occur to form additional hydrogen and carbon monoxide, particularly at high temperatures and in the presence of active catalysts.

The reaction of carbon dioxide with methane may be important commercially.[22a] In an example, gas resulting from the hydrogenation of coal, tar, or mineral oil and containing 30 to 40 per cent methane is mixed with carbon dioxide to have the following percentage composition: carbon dioxide 23.6, hydrogen 52, methane 22.5, nitrogen 1.3, and carbon monoxide 0.6. This mixture is passed at 1100° C. through a reactor furnace with refractory lining and refractory filling on which nickel or other catalyst is deposited. Waste gas is used for heating. The product contains carbon monoxide 31.4 per cent and hydrogen 66.2 per cent together with small amounts of carbon dioxide and nitrogen, and may be further treated, with steam to convert the carbon monoxide to hydrogen. At this temperature (1100° C.) the free energy equation for reaction (3) shows that equilibrium is practically completely to the right. Whether such conversion is capable of realization in practice is, of course, open to question, since secondary reactions would so complicate the results as to make a mechanism analysis difficult.

Experimental data for the reaction are furnished by the results of some recent work by Klyukvin and Klyukvina.[22b] With a 1 : 1 mixture of

[22] a. Brit. Pat. 279,072 (1927 published) I. G. Farbenind.; *compare also*, Peters & Pranschke, *Brennstoff Chem.* 11, 473-6 (1930); b. Klyukvin and Klyukvina, *J. Chem. Ind. (Moscow)* 7, 743-52 (1930); c. Pichler, *Z. angew Chem.*, June 6, 1931, p. 472.

carbon dioxide and methane passed over a reduced nickel catalyst at 1000° C: these workers obtained a conversion of 97.6 per cent methane, which resulted in a gaseous product comprising 47 per cent carbon monoxide, 48.6 per cent hydrogen, 2.6 per cent nitrogen, and no by-products. Under the same conditions but without catalysts 43 per cent methane was converted in porcelain tubes and 58 per cent in iron tubes. The time of contact was about 38 seconds. These results show that at high temperatures and in the presence of active catalysts the reaction furnishes a feasible means for obtaining hydrogen and carbon monoxide mixtures, and substantiate the claims made in patents for the process.

It is to be noticed that reaction (3) occurs with a twofold increase in volume and would, hence, be suppressed by the application of pressure. This has been demonstrated experimentally by Pichler,[22c] who also worked with a nickel catalyst. At a pressure of one atmosphere a temperature of 900° C. was required to force the reaction to completion to the right. However, at a pressure of 0.01 atmosphere complete conversion of methane was obtained at 500° to 600° C. Further reduction in pressure resulted in a still lower temperature being required for good conversions of methane. Furthermore, reaction velocity was found to increase in proportion to the decrease in pressure.

If a source of carbon dioxide and methane is available, such as is implied in the foregoing experiments, then a process for the formation of hydrogen and carbon monoxide by this means might prove economically advantageous. The use of flue gas as a source of carbon dioxide would lead to the introduction of nitrogen in undesirable quantities if the gas is to be used for methanol synthesis, although it might prove advantageous in the case of production of hydrogen for ammonia synthesis. The carbon dioxide obtained by the scrubbing of converted water-gas in the production of hydrogen could be used and would not lead to the introduction of nitrogen.

From a consideration of the equilibrium of reaction (3) as a function of temperature (Fig. 14), it is noticed that this reaction occurs readily to the right at temperatures of 900° to 1000° C. The $(CO_2 + CH_4)$ reaction is catalyzed by substances similar to those used for the methane-steam reaction, i.e., 90 per cent nickel oxide-10 per cent thoria, etc. A combination of reaction (2) and reactions (3) and (4) may, hence, be considered as a means of producing hydrogen and carbon monoxide mixtures; or by use of the water-gas catalytic reaction, (6), of producing hydrogen. A combination of these reactions thus becomes:

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$CO_2 + CH_4 = 2CO + 2H_2$$
$$2H_2O + 2CH_4 = 2CO + 6H_2$$
$$\overline{4CH_4 + 2O_2 = 4CO + 8H_2,} \text{ or}$$
$$2CH_4 + O_2 = 2CO + 4H_2 \tag{1}$$
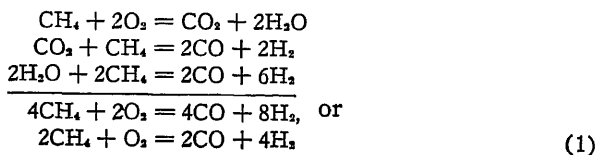
Such a combination of reactions may thus be made to produce hydrogen and carbon monoxide mixtures in the proportions required for methanol synthesis, $2H_2 : 1CO$.

While reactions (3) and (4) are both highly endothermic, reaction (2) is exothermic and may be used to furnish heat for the combined process. The net heat effect of reaction (1), is such that if no heat losses occurred, the process would be self-supporting. The use of excess oxygen over that theoretically required could be made the means for supplying heat losses.

In practice, however, oxygen would be too expensive to use in the pure form and air would have to be used as a source. This means that nitrogen would be introduced and. the final mixture, assuming stoichiometric proportions, would consist of $2CO : 4H_2 : 3.8N_2$. With excess air the proportions of nitrogen would be even higher.

If such a mixture were to be used for methanol synthesis a considerably higher pressure than usual would be necessary to allow for the dilution of the reacting gases by the nitrogen. Furthermore, high losses of hydrogen and carbon monoxide would result due to bleed off of nitrogen to prevent its accumulation in the recycled gases. For these reasons alone the process loses its attractiveness.

By introducing water, cooling the hot gases from approximately 1000° C. to 500° C., and passing this steam, hydrogen, carbon monoxide, nitrogen mixture over suitable catalysts, the carbon monoxide may be oxidized to carbon dioxide and an extra mol of hydrogen formed per mol of carbon monoxide. On the assumption that complete conversion would be obtained and that stoichiometric proportions of the reactants have been used, a mixture comprising $6H_2 : 3.8N_2$ would result. Such a mixture is too lean in hydrogen for ammonia conversion, and if used as such would be open to the same objections as in the methanol conversion just discussed. Enrichment with hydrogen would introduce other complicating factors pertinent to production of this hydrogen.

For the purpose of obtaining nitrogen-hydrogen mixtures suitable for ammonia synthesis, methane may be subjected to partial combustion with air and the carbon monoxide converted to hydrogen in the water-gas process. Thus, by burning suitably preheated mixtures consisting of 10 parts by volume of coke oven gas containing 30 per cent of methane with sufficient air to give about 3 parts by volume of oxygen under such conditions that the exit gases are at a temperature of 1200° to 1300° C. and converting the carbon monoxide with steam, it is claimed to be possible to obtain mixtures of nitrogen and hydrogen which, after purification, are suitable for ammonia synthesis.[23]

For the purpose of utilization in the formation of hydro-oxygenated compounds of carbon, methane is partly burned so as to obtain a gaseous

[23] Brit. Pat. 231,218 (1925) Badische Anilin u. Soda Fabrik; Ger. Pat. 507,917 (1926) I. G. Farbenind.

mixture containing two mols of hydrogen per mol of carbon monoxide.[24] For utilization in ammonia synthesis, however, the combination of oxidation by steam and oxygen at temperatures of about 1000° C. is better adapted for the production of hydrogen since better conversion to hydrogen alone is possible.

OXIDATION OF METHANE WITH STEAM

The reaction of hydrocarbons with steam to form hydrogen has received more attention than any of the other methods for producing hydro-
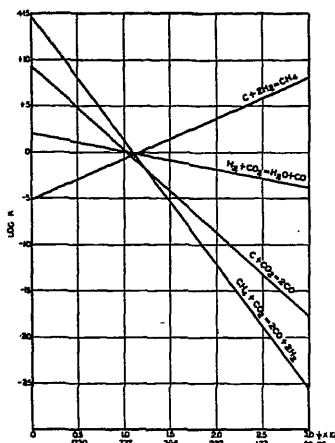
FIG. 14.—Equilibrium as a function of temperature for several reactions involved in the oxidation of methane with carbon dioxide.
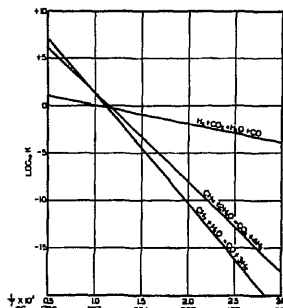
FIG. 15.—Equilibrium as a function of temperature for reactions involved between methane and steam.

gen from low molecular weight hydrocarbons by oxidation. Although a number of patents have been granted on processes of this type,[25] relatively little information is to be found in the general literature. No data are available on commercial operations of these processes either in this country or abroad. It is rather interesting to note, however, that one of the larger oil companies operating in this country, through its subsidiary development company, is entering the synthetic ammonia industry with an estimated daily capacity of 80 tons of ammonia.[26] This company has installed a plant for the production of the necessary hydrogen by the thermal decomposition of methane. Also, if one is to judge from the patents issued to the originators and present exploiters of the recent hydrogenation of

[24] Can. Pat. 264,600 (1926) Patart; Brit. Pats. 266,405 and 266,410 (1927) Badische Anilin u. Soda Fabrik.
[25] a. Dieffenbach and Moldenhauer, Ger. Pat. 229,406 (1909); b. Badische Anilin u. Soda Fabrik, Brit. Pat. 12, 978 (1913); Ger. Pat. 296,866 (1919); Brit. Pat. 266,410 (1927); U.S. Pat. 1,128,804 (1915) Mittasch and Schneider; c. Bergius, Brit. Pat. 244,730 (1924); Can. Pat. 263,477 (1926); d. I. G. Farbenind., Brit. Pat. 265,989 (1926); 267,535 (1926).
[26] *Ind. Eng. Chem., News Ed.* **8**, No. 13, 13 (1930).

coal and oil processes, the utilization of methane or other "waste" hydrocarbons as a source for the hydrogen is a fact.[*] Boomer [27] states that the conversion of Alberta natural gas is being considered as a source of hydrogen and carbon monoxide for high pressure synthesis of hydro-oxygenated compounds of carbon.

Since the first successful experimentation by Sabatier and Senderens,[28] a number of workers have studied the reaction (4). The equilibrium for this reaction:

$$CH_4 + H_2O = CO + 3H_2 \tag{4}$$

has been experimentally determined as a function of temperature by Newmann and Jacob.[29] Equilibrium was approached from both directions and the determined values are in general agreement with the values calculated from free energy data:

$$\log K_4 = -\frac{10308}{T} + 4.87 \log T + 0.000066T - 0.000000081T^2 - 3.04$$

where:

$$K_4 = \frac{p_{CO} \times p^3_{H_2}}{p_{CH_4} \times p_{H_2O}}$$

Figure 16 shows the values obtained from the theoretical equation.

It may be seen from the curve that the reaction does not occur to any appreciable extent below about 350° C., and that a temperature of about
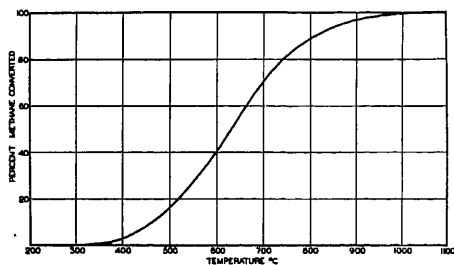
FIG. 16.—Conversion of methane to hydrogen and carbon monoxide at equilibrium by an equimolar amount of steam.
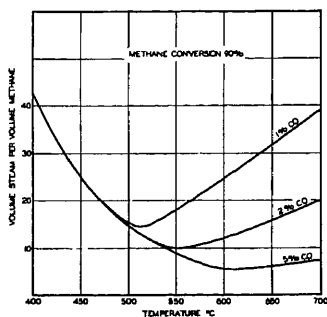
FIG. 17.—Steam necessary to convert methane to hydrogen with different amounts of carbon monoxide present in the final gas.[31]

1000° C. is necessary for its practical completion. The decomposition of methane with steam goes quantitatively at 1300° C. to form hydrogen and carbon monoxide. It is possible, however, by using an excess of steam to force the reaction to the right and thus to obtain good conversion to

[*] Haslam and Russell, *Ind. Eng. Chem.* **22**, 1030 (1930).
[27] *Ninth Annual Rept. Sci. Ind. Res. Council Alberta*, 1928, 51-3.
[28] Sabatier and Senderens, *Compt. rend.* **134**, 514-689 (1902).
[29] Newmann and Jacob, *Z. Electrochem.* **30**, 557 (1924).

hydrogen at lower temperatures. The use of excess steam is also desirable from the standpoint of preventing the deposition of carbon, which is noticeable when only theoretical steam is used.

It should be noted that when natural or refinery gas containing substantial proportions of hydrocarbons higher than methane, is used for conversion to hydrogen, considerable difficulty may be encountered by the deposition of carbon on the catalyst. The high temperatures necessary to employ for the methane-steam reaction is such as to induce the complete thermal decomposition of the higher hydrocarbons or their intermediate decomposition products with resulting carbon deposition. This extremely objectional occurrence results in rapid catalyst deterioration and necessitates frequent renewal or reactivation. By suitably restricting the composition of the hydrocarbon gas used, by controlling the temperature of the catalyst and by using an excess of steam this feature may be mitigated to such an extent as to enable the process to be used industrially.

The reaction of steam with carbon according to:

$$C + 2H_2O = CO_2 + 2H_2$$
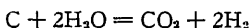
occurs with a measurable velocity at temperatures above 400° C. and has an equilibrium constant

$$K = \frac{p^{\frac{1}{2}}_{CO_2} \times p_{H_2}}{p_{H_2O}}$$

equal to 1 at a temperature of about 480° C.[30]
The reaction:

$$C + H_2O = CO + H_2$$
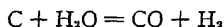
is much slower and does not have as favorable an equilibrium at temperatures below 725° C.

To obtain good conversion by reaction (4) even with an excess of steam it is necessary to use an active catalyst in order to operate at a temperature lower than 1000° C. Nickel catalysts, promoted with alumina or thoria and supported on fire clay, magnesium oxide, or brick, are very suitable for the process, giving essentially equilibrium conversion at low rates of gas flow through the converter. At increasing rates of flow the increase in unconverted methane is practically linear with the increase in space velocity.*

By operating the process at a lower temperature with a larger proportion of steam it is possible to obtain reaction to carbon dioxide according to:

$$CH_4 + 2H_2O = CO_2 + 4H_2 \tag{5}$$

By this reaction it is possible to obtain four mols of hydrogen per mol of methane in contrast to the three mols of hydrogen and one mol of carbon

[30] Haslam and Russell, "Fuels and their Combustion," New York, McGraw-Hill Book Co., Inc., 1926, p. 162.

* Space velocity $= \dfrac{\text{vol. gas measured at standard conditions}}{\text{(vol. catalyst) (hour)}}$

monoxide possible according to reaction (4). It must not be overlooked, however, that it is possible for these two reactions, (4) and (5), to be in equilibrium with each other through the water-gas catalytic reaction:

$$CO + H_2O = CO_2 + H_2. \tag{6}$$

Thus, reaction (5) is really the sum of reactions (4) and (6) as:

$$CH_4 + H_2O = CO + 3H_2 \tag{4}$$
$$CO + H_2O = CO_2 + H_2 \tag{6}$$
$$\overline{CH_4 + 2H_2O = CO_2 + 4H_2} \tag{5}$$
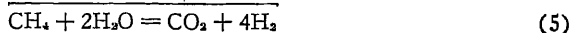
If the catalyst used in the process is active in promoting both reaction (5) and the water gas reaction, it is perfectly possible that the proportion of reaction going according to (4) and (5) will be governed by the water-gas equilibrium. Since reaction (5) is a trimolecular reaction as written it is also quite possible that it occurs in steps represented by reactions (4) and (6) so that it is essential to employ a catalyst active in promoting the water gas reaction in order to realize the reaction at all quantitatively.

Data on this phase of the process is obtainable from a patent granted to Blake.[81] Consideration of this data shows that carbon monoxide and carbon dioxide are present in the proportions required for the water-gas equilibrium (6). Figure 17 shows a portion of this data graphically and gives the ratio of steam to methane necessary for 90 per cent methane conversion with different amounts of carbon monoxide remaining in the gas.

The catalytic water-gas reaction and equilibrium is represented by the equation:

$$\log K_6 = \frac{2210}{T} - 0.9103 \log T + 0.000974T - 0.000000149T^2 - 0.118,$$

where:

$$K_6 = \frac{p_{CO_2} \times p_{H_2}}{p_{CO} \times p_{H_2O}},$$

which may be obtained from free energy data. Table XVII shows the change in the equilibrium constant with temperature for this reaction. These values show that as the temperature increases, equilibrium shifts in

TABLE XVII.—*Water-Gas Reaction Equilibrium.*

T° C.	T° K.	K_6
400	673	15.17
450	723	9.16
500	773	5.88
600	873	2.96

favor of carbon monoxide. Hence, in order to react methane with steam to form carbon dioxide and hydrogen, it is essential that the operation be at a temperature of about 500° to 600° C. However, as consideration of

[81] U.S. Pat. 1,713,325 (1929) Blake assr. to Lazote, Inc.

the free energy equation for reaction (5) will show, the conversion becomes objectionably low at these lower temperatures. It is also necessary to employ more active catalysts which are more susceptible to poisoning for operation at lower temperatures. It is claimed that operating temperatures as low as 300° C. may be realized by the use of iron, nickel, or cobalt catalysts activated with the oxides or other compounds of metals whose oxides are difficultly reducible such as chromium, vanadium, alkali, and alkali earth metals.[32] However, no mention is made to resistance to poisoning of these catalysts.

The equilibrium constant for reaction (5), may be calculated from free energy data,[17] by means of the equation:

$$\log K_5 = -\frac{8100}{T} + 3.96 \log T + 0.00104T - 0.00000023T^2 - 3.15$$

where

$$K_5 = \frac{p_{CO_2} \times p^4_{H_2}}{p_{CH_4} \times p^2_{H_2O}}$$

In verifying the theoretical values for equilibrium, Pease and Chesebro[33] have shown that at 500° C., 28.6 per cent of the methane is converted when theoretical steam is used.

TABLE XVIII.—*Equilibrium Constants.*

T °C.	T °K.	K_4	K_5
500	773	0.00482 *	0.0300 *
600	873	0.2990 *	0.897 *
700	973	7.890 *	14.25 *
800	1073	150.5 **	
900	1173	1296.**	
1000	1273	7940.**	

* Calculated.
** Hawk, Golden, Storch and Fieldner.

The experimental results are in excellent agreement with the calculated values, and apparently justify the use of this free energy equation and the free energy value for methane given by Lewis and Randall at temperatures in the neighborhood of 500° C.

By carrying out the steam-methane reaction in stages at temperatures of 400° to 600° C. with intermittent removal of carbon dioxide, it is possible to convert almost completely according to reaction (5).[34] For removal of carbon dioxide use may be made of the oxides of metals, the carbonates of which have a dissociation temperature which is not sufficiently high to make regeneration difficult. The temperature for absorption of carbon dioxide is somewhat lower than reaction temperature being about 110° C. in the case of cerous oxide and 350° C. in the case of lime. For regeneration of the oxide from the carbonate it is necessary to heat to 350° to 500° C. in the case of cerium; in the case of lime regeneration

[32] Brit. Pat. 267,535 (1927) open to inspect. I. G. Farbenind.
[33] Pease and Chesebro, *J. Am. Chem. Soc.* 50, 1464 (1928).
[34] *Cf.* Brit. Pat. 291,244 (1928) I. G. Farbenind.

may or may not be essential depending on local conditions for utilization of carbonate and availability of lime. The advantages of this modification of the process are obvious from the standpoint of methane utilization for hydrogen production, but the disadvantages of operating a process which at best could be only semi-continuous and which requires either regeneration of the absorbent or else a very cheap supply, are equally obvious.

Under equilibrium conditions a mixture of one volume of methane and two volumes of steam at 500° C. and one atmosphere of pressure will give a dry gas mixture consisting of 60 per cent hydrogen, 38 per cent methane, and 2 per cent carbon monoxide. The hydrogen may be purified from methane, water, carbon oxides, oxygen, etc., by low temperature fractionation or by suitably absorbing the undesirable constituents with either solid or liquid absorbents. The use of low temperature fractionation requiring refrigeration as by the Linde process is not satisfactory because of the high installation cost of such a system. Hence, the absorption processes are most generally used.

Because of the several objectionable features attending the methane-steam reaction to form carbon dioxide and hydrogen directly, viz., the necessity for operating at a low temperature at a low reaction rate and with a highly active and sensitive catalyst, the necessity for the use of large excesses of steam to force the reaction, and the difficulty of obtaining practically complete conversion of methane, the step-wise process of first converting to carbon monoxide and hydrogen at a high temperature and of then oxidizing the carbon monoxide by the water-gas catalytic reaction at a lower temperature is the more applicable to commercial use.

The reaction to form hydrogen and carbon monoxide has the disadvantages of requiring a high temperature and of requiring large quantities of heat, since it is endothermic. Besides supplying the sensible heat to the reactants, it is necessary to furnish about 5000 calories per gram mol of methane reacting. The necessity of supplying this heat at a high temperature level and of operating at temperatures so high that the steam corrosion becomes an important factor makes the design of equipment difficult. The use of direct fired, metallic catalyst tubes is not possible and other means of heating and maintaining a high temperature have been devised.

It is possible to supply the necessary heat directly to the reacting steam and methane by burning a portion of the combustible materials present with air or oxygen which is admitted with the reaction mixture or at intervals along the reaction chamber. Difficulty, however, has been encountered with catalyst poisoning when air or oxygen is admitted directly with the methane-steam mixture for purposes of heating. This is especially noticeable when such catalysts as activated nickel are used to promote the methane-steam reaction. This poisoning action is very similar to that noticed with the promoted iron-alumina catalysts used in the synthesis of ammonia from mixtures of hydrogen and nitrogen, and is probably caused

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by the formation of films of oxide at the catalyst surface which destroy the activity. This objection may be overcome, however, by using certain proportions of hydrogen or carbon monoxide, or both, admixed with the steam-methane-air mixture. Reaction of oxygen with these admixed reducing gases is very rapid and begins to occur at relatively low temperatures to liberate large quantities of heat. The reducing action is sufficiently powerful to prevent the formation of the oxide film on the nickel and the activity of the catalyst preserved. The relative proportion of this added heating material will necessarily depend upon the equipment used and the temperature necessary to maintain in the reactor.

To eliminate the difficulties attending the intermittent addition of oxygen or air to the reacting steam and methane, the necessary combustion may be permitted to occur in a separate step * and the resulting hot gaseous mixture is then passed directly to the catalyst for effecting the conversion. The process would thus be a step-wise one with the two steps carried out in succession as follows:

1. The partial combustion of methane with oxygen in order to raise the temperature and secure sufficient heat for the second step.

2. The catalytic decomposition of the remaining methane with steam to form carbon monoxide and hydrogen.[35]

Surface appears to be the most important variable in the operation of the first step as has been seen already and broken pieces of refractory may be used to catalyze the reaction. Surface appears to accelerate the reaction to complete combustion to water and carbon dioxide so that as the surface is increased, the proportion of hydrogen and carbon monoxide decreases and the proportion of unreacted methane increases together with the water and carbon dioxide. To raise the temperature of the gases to 1000° to 1100° C., the ratio of inlet oxygen to methane by volume may vary from about 65 to 75:100. The presence of water has only a slight effect on the reaction and may be added at this point for the purpose of heating for the second step.

The methane-steam reaction requires an active catalyst even at temperatures of 1000° to 1100° C. as has been pointed out already. With a suitable catalyst and time of contact it is possible to obtain practically complete conversion of the methane to hydrogen and carbon monoxide at this temperature. Excess steam above that required for suppression of carbon deposition, about 60 mols total steam to 40 mols of methane, forces the water-gas reaction and carbon dioxide formation may result.

Such combustion processes for the purpose of furnishing heat directly to the reactants as have just been described are handicapped by the necessity for using expensive oxygen or by the introduction of nitrogen if air is used. Although the introduction of nitrogen in this way may not be

* Reference should be made to Hawk, Golden, Storch, and Fieldner (U. S. Bur. of Mines), presented at Am. Chem. Soc. meeting at Buffalo, Sept. 1 and 2, 1931.
[35] In this regard *see* Brit. Pats. 288,662 (1928), 301,969 (1928) I. G. Farbenind.; Pol. Pat. 10,425 (1930) *Chem. Zentr.* 1930, II, 1641; Ger. Pat. 435,588 (1926) Bergius; Brit. Pat. 349,067 (1930) Soc. Etudes Scie. et Entrepr. Industr. Voituron.

objectionable if the hydrogen is to be used for ammonia synthesis, particularly not if correct amounts may be introduced, it is objectionable when the hydrogen is to be used for alcohol synthesis or pressure hydrogenations because of its diluent effect. Hence, it is advantageous in some instances to make use of an intermittently heated checkerwork in a manner similar to that used in the Thermatomic carbon process, already described.* In such a process, mixtures of hydrocarbon gas or other fuel and air, and of hydrocarbon gas and steam are passed alternately into the reaction chamber which is packed with a checkerwork of fire-brick containing the catalyst. This checkerwork is thus first heated by the burning gaseous mixture and then cooled by the reaction of the steam-methane mixture. The use of suitable heat exchange and recovery makes it possible to use the heat of the hot reaction products to preheat the incoming steam and methane which it is desired to react. Such a process may be operated with good thermal efficiency and air may be used for combustion.

Where hydrogen is desired, it is necessary to oxidize the carbon monoxide by further reaction with steam through the water-gas catalytic reaction since by this means an extra mol of hydrogen is obtained per mol of carbon monoxide present in the gas.

This third step, the water-gas catalytic reaction, gives off about 10,000 calories per mol of carbon monoxide reacting at temperature of 500° C. By a proper use of heat exchange and insulation it is, therefore, possible to make this reaction autothermal. Since the reaction is exothermal, low temperatures favor complete carbon monoxide conversion, but also give slow reaction rates unless very active, highly sensitive catalysts are used. However, the use of excess steam forces the water-gas reaction to the right so that with a steam to water-gas ratio of 3 : 1 the carbon monoxide present at equilibrium after condensation of water is 2 per cent at 550° C., 1 per cent at 445° C., and 0.5 per cent at 380° C. Excess steam may be used in this reaction to force the carbon monoxide content of the gas to a very low value as shown in Figure 18 which gives the ratio of minimum volumes of steam to volumes of dry water-gas of the composition:

		Per Cent
Hydrogen	....	49.2
Carbon monoxide	....	41.3
Carbon dioxide	....	4.2
Methane	....	0.8
Nitrogen	....	4.5

necessary to reduce the carbon monoxide content to 1.5 per cent in the dry effluent gas at various temperatures.

The reaction does not occur at 550° C. without a catalyst and at 400° C. requires an active catalyst for good conversion. The reaction goes readily at 500° C. in the presence of iron catalysts promoted with alumina

and potassium oxide.[86] The use of alumina as a promoter for a nickel catalyst has been found to favor carbon dioxide formation in the catalytic oxidation of methane with steam,[87] showing that it promotes the water-gas reaction. The use of magnesia in a like capacity favored the forma-

Fig. 18.—Steam necessary to convert water gas to a carbon monoxide content of 1.5 per cent at atmospheric pressure equilibrium.

tion of carbon monoxide, indicating that it is without effect in promoting the water-gas reaction. A number of patented catalysts are mentioned by Taylor.[88]

It is claimed that the use of pressure makes it possible to increase the rate of the water-gas catalytic reaction.[89] Since the reaction occurs without any change in volume, the equilibrium conversion at a given temperature will not be affected by an increase in pressure, excepting in so far as the gaseous reactants may deviate from the gas laws in their behavior; but as the reaction is necessarily a catalytic process, the use of pressure may affect changes in the adsorption of the reactants at the catalyst surface in such a manner as to give an increase in the rate.

A more satisfactory arrangement for obtaining higher reaction rates consists in the use of two reactors in series. The first of these is operated at a high temperature and in it the reaction velocity is consequently high. The conversion, however, is not complete at this high temperature due to the unfavorable equilibrium and about 5 to 6 per cent of carbon monoxide may remain in the exit gas. The second reactor is maintained at such a temperature that the conversion gives an exit gas of from 1 to 2 per cent carbon monoxide without requiring the addition of any more steam.

Since carbon dioxide is roughly fifty times as soluble in water as hydrogen it is readily separated from the exit gas from the last convertor by scrubbing with water. As the solubility increases rapidly with pressure without greatly affecting this ratio, it is common practice to scrub under a pressure of about 30 atmospheres, a process which entails but a small loss of hydrogen. The selection of the proper pressure for conducting this step is a matter of economic balance and the actual pressure used will, hence, depend upon conditions existing at the particular plant. Somewhat over half of the energy required for pumping the water is recovered by releasing the carbon dioxide solution through Pelton wheels. This opera-

[86] Evans and Newton, *Ind. Eng. Chem.* 18, 513-17 (1926).
[87] Kubota and Yamanaka, *Bull. Chem. Soc. Japan* 4, 211-20 (1929). *Compare* Brit. Pat. 279,128, Bomke assr. to Eisen u. Stahlwerke Hoesch.
[88] Taylor, "Industrial Hydrogen," New York, Chemical Catalog Co., Inc., 1921, p. 158; also *J. Phys. Chem.* 29, 1325 (1925).
[89] U.S. Pat. 1,157,669 (1915) Bosch and Wild assrs. to Badische Anilin u. Soda Fabrik.

tion at the same time strips the water of carbon dioxide so that it may be reused.

The solubility of carbon dioxide in water as a function of pressure as given by the data of Hachnel [40] is shown in Table XIX.

TABLE XIX.—*Solubility of Carbon Dioxide in Water.*

Vols. of CO_2 (at 0° C. and 760 mm.)

Pressure in Atmospheres	Vol. of Water	
	15° C. (Seidel)	20° C. (Intl. Crit. Tables)
1	1.0	...
5	4.59	...
10	8.39	...
15	11.85	...
20	15.21	...
25	17.64	16.3
30	20.31	18.2
35	22.52	20.1
40	24.44	22.0
45	....	23.9
50	....	25.7

When the hydrogen is to be used for the synthesis of ammonia, it is necessary that the carbon monoxide be completely removed from the gas since it acts in a manner similar to water vapor in poisoning the ammonia catalysts. Even with a large excess of steam present and operation so that equilibrium is practically obtained in the water gas catalytic reaction all of the carbon monoxide is not converted to carbon dioxide. It is, hence, necessary to resort to other means for removing the last trace of monoxide. This may be accomplished by scrubbing at a pressure of about 200 atmospheres with such absorbents as aqueous solutions of cuprous ammonium carbonate or formate. The use of cuprous ammonium chloride solutions is prohibitive on account of corrosion difficulties. The copper solution is regenerated by heating under a vacuum after it becomes no longer effective. One advantage of this scrubbing operation is the fact that not only is the carbon monoxide content of the gases reduced to a negligible amount, but the remaining oxygen and carbon dioxide from the 25 to 30 atmosphere pressure water scrubbing operation are also removed. Notwithstanding that it is in widespread use, this is a somewhat unsatisfactory procedure and attempts have been made to oxidize the carbon monoxide with oxygen preferentially to carbon dioxide which may then be readily scrubbed out with water.

Present practice in the Haber-Bosch process for utilizing water-gas in ammonia synthesis results in the production of a gas containing 1 to 2 per cent carbon monoxide, a concentration too high to be removed practically in a catalytic preferential oxidation process because of reduction

[40] Hachnel, Seidel, "Solubilities of Inorganic and Organic Compounds," New York, D. Van Nostrand Co., Inc., 1928, Vol. II, p. 1155. International Critical Tables 3, 260 (1928).

of the oxide catalysts by hydrogen, with consequent destruction of catalytic activity and loss of hydrogen. For carbon monoxide concentrations not exceeding 0.5 per cent the process is practical [41] since the difficulties of heat dissipation may be overcome. For this purpose metallic oxide catalysts, singly or in mixtures of two or more are used. Multiple component hopcalites (mixtures of finely divided manganese dioxide with such metallic oxides as those of copper, cobalt, silver, iron, etc.) have been found suitable for the oxidation of carbon monoxide to carbon dioxide with air or oxygen at ordinary temperatures.[42] These mixed catalysts exhibit the remarkable effects that may be obtained through "promoter action" since the oxides taken singly do not give at all comparable results. It apparently makes little difference whether the metallic oxides are prepared by mixing the moist hydrates or by stirring together finely ground portions of the previously dried or ignited components, and the conclusion has been drawn that the mixture effect is due to a speeding up of the electronic rearrangement which has been postulated in the mechanism for the catalytic reaction.[43] No evidence of compound formation has been noticed between the well-washed oxides of copper and manganese when mixed.[44]

The preferential oxidation process consists of adding sufficient air to the mixed gas to give a slight excess over that required for the oxidation of the monoxide, saturating the mixture with water vapor at a temperature somewhat above room (about 40° C.) and passing it over the catalyst contained in narrow bore copper tubes immersed in a temperature controlled liquid bath. The water vapor exhibits a selective poisoning action toward hydrogen oxidation,[45] apparently independent of concentration and of catalyst temperature.

Because of this effect of water vapor, Kuentzel [46] has been led to believe that by using higher amounts of steam to give better temperature control and prevent local overheating, concentrations of 1 to 2 per cent of carbon monoxide could be efficiently oxidized. It was found that a 2-component hopcalite composed of 60 per cent manganese dioxide and 40 per cent cupric oxide would give an efficiency of 96 per cent for a period of thirty-seven hours, when used at a temperature of 175° C. with a large excess of steam. Catalysts such as copper oxide, manganese dioxide, and a 5-component hopcalite, although giving high initial conversions, rapidly deteriorated through reduction. With a converted water-gas of the composition:

[41] a. Harger and Terry, Brit. Pat. 127,609 (1917); U.S. Pat. 1,366,176 (1921); b. Rideal and Taylor, Brit. Pat. 129,743 (1918); U.S. Pat. 1,375,932 (1921); c. Frazer, Lamb, and Merrill, U.S. Pat. 1,418,246 (1922); d. Rideal, *J. Chem. Soc.* 115, 993 (1919); e. Lamb, Scalione and Edgar, *J. Am. Chem. Soc.* 44, 738 (1922); f. Harrison and Baxter, *Phil. Mag.* (7), 3, 31-50 (1927).
[42] a. Lamb, Bray, and Frazer, *J. Ind. Eng. Chem.* 12, 213 (1920); b. Rogers, Piggot, Bahlke, and Jennings, *J. Am. Chem. Soc.* 43, 1972 (1921); c. Merrill and Scalione, *J. Am. Chem. Soc.* 43, 1982 (1921); d. Frazer and Scalione, U.S. Pat. 1,345,323 (1920).
[43] Hoskins and Bray, *J. Am. Chem. Soc.* 48, 1454 (1926).
[44] Draper, *ibid.* 50, 2637 (1928).
[45] Lamb and Vail, *J. Am. Chem. Soc.* 47, 123 (1925).
[46] *J. Am. Chem. Soc.* 52, 437-44; 445-55 (1930).

	Per Cent
Carbon monoxide	1.3
Oxygen	1.5
Carbon dioxide	28.0
Hydrogen	49.0
Nitrogen	20.2

and in the presence of three volumes of steam per volume of gas, a space velocity of 1000 was found suitable in the temperature range of 160° to 195° C. The large excess of steam with its large heat capacity functions as a very effective dissipator of heat and obviates the necessity for using a high heat conducting catalyst chamber. The steam further lengthens the life of the catalyst by inhibiting reduction by the hydrogen through an unexplained poisoning action.

The kinetics of the heterogeneous reaction between carbon monoxide and oxygen on the surface of quartz has been studied by Bodenstein and Ohlmer.[47] The velocity of the reaction varied in direct proportion to the pressure of oxygen and in inverse proportion to the pressure of carbon monoxide itself. This effect has been interpreted by the adsorption theory as due to the strong adsorption of the carbon monoxide and the slight adsorption of oxygen. The amount of uncovered space left on the active surface is inversely proportional to the pressure of the carbon monoxide, and the rate of reaction is, therefore, proportional to the pressure of oxygen or the rate at which it is adsorbed at the surface. It is not sufficient for reaction that an oxygen molecule strike an adsorbed carbon monoxide for this would simply make the rate of reaction independent of the monoxide concentration. For reaction to occur oxygen must be adsorbed on that portion of the surface left free by the carbon monoxide.

Such relationships as are shown here are important in showing that it is frequently essential for both reactants to be adsorbed at the catalyst surface before reaction can occur. More than mere collision between a free and an adsorbed molecule is necessary in such instances.

Low pressure experiments on the reaction between oxygen and carbon monoxide at platinum surfaces have been made by Langmuir.[48] Up to temperatures of 700° K. the reaction proceeded in accord with Bodensteins' results, but at temperatures between 750° and 1050° K., the nature of the reaction changed so that the velocity was proportional to the pressure of the constituent present in least amount.

These results are of primary interest here in showing the nature of the reaction when conducted in the presence of certain catalysts. In the actual practice of preferential combustion of carbon monoxide in the presence of large excesses of hydrogen and water vapor extremely selective catalysts are necessary, and it would be interesting to compare the absorptive capacities of some that have been used.

Although cost figures for the production of hydrogen by the methane-

[47] *Z. physik. Chem.* **53**, 166 (1905).
[48] *Trans. Faraday Soc.* **17**, 621 (1922).

steam reaction are not directly available, the fact that four volumes of hydrogen may be obtained per volume of methane reacted gives the process considerable interest industrially. In locations where both water and cheap natural gas are available it should be possible to produce hydrogen at very low cost. The possibility of burning methane with air as a source of heat and power and then scrubbing out the carbon dioxide from the flue gases should at the same time make available cheap nitrogen. In this way the raw materials for ammonia synthesis should be available at low cost. Also, the methane available in refinery gases, coke oven gas, and in the
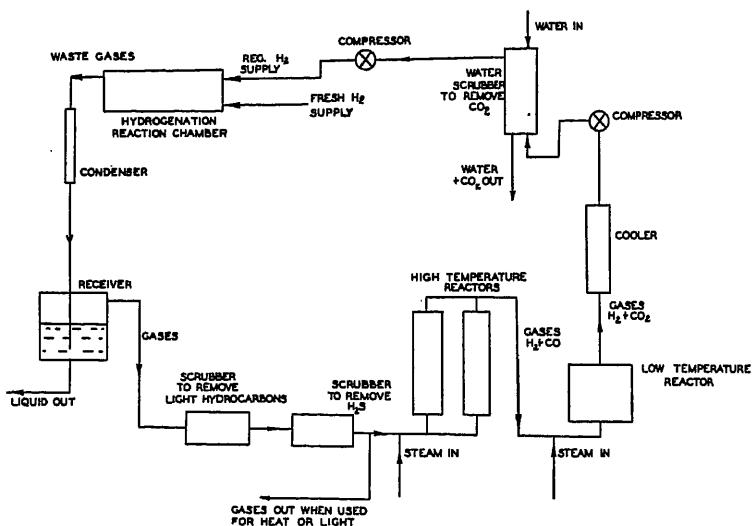
FIG. 19.—Schematic layout for plant recovering hydrogen from waste gases from hydrogenation plant.

by-product gases from the high pressure hydrogenation of coal and oil is being considered for reaction with steam to produce hydrogen for use in either the hydrogenation processes itself [49] or in other high pressure processes.[50] Figure 19 shows a schematic layout for a plant to recover hydrogen from the hydrocarbon waste gases of the hydrogenation process. It will be noted that no provision is made for the removal of carbon monoxide remaining in the hydrogen. This is not necessary when the hydrogen is used in the hydrogenation of coal or oil since no poisoning action is found to occur.

Natural gas reformed in water-gas generators is also suitable for use as city gas as for mixing with manufactured gas.[51]

[49] Bergius, Brit. Pat. 244,730 (1924); Can. Pat. 263,477 (1926); U.S. Pat. 1,699,177 (1929).
[50] Fr. Pat. 644,148 (1927) I. G. Farbenindustrie.
[51] For a discussion *see U. S. Bur. Mines Rep. Investigations* No. 2973.

Chapter X

Surface Combustion

In general, surface combustion involves the rapid and complete burning of explosive gas or vapor-air mixtures in theoretical proportions for complete combustion, *without flame* and at the surface of an incandescent solid. More specifically from an industrial viewpoint, it involves such a burning process in the interstices of a porous refractory block or at the surface of broken bits of porous refractory. It represents a very efficient means of securing combustion since none or very little excess air is required and since the transfer of heat can be made to occur largely by radiation from the hot solid. Although liquid fuels have been used in certain adaptations, industrial gases furnish the bulk of the combustible used. Because of the relative cleanliness of the process, accuracy of control, concentration of heat source, and high temperatures attainable, surface combustion has found application in a variety of manufacturing processes.

Historical

After he had discovered that combustible gases could be made to combine with oxygen at temperatures below their ignition point during the course of some experiments made in developing the first safety miners' lamp, Sir Humphry Davy was led to try whether the heat of such flameless combustion could be sufficient to cause the incandescence of solids suspended in the mixture. Thus, in 1817 he discovered that a warm platinum wire inserted in a container filled with a non-explosive mixture of coal gas and oxygen became red hot and continued so until nearly all of the oxygen had been consumed from the excess of coal gas. In continuing his experiments Davy found that mixtures of oxygen with other combustible gases such as ethylene, carbon monoxide, hydrogen, or hydrogen cyanide behaved in a similar manner and that palladium behaved as did platinum but that silver, gold, copper, or zinc wires did not glow.

These discoveries stimulated other research workers to activity and in the following period from 1819 to 1836 considerable attention was devoted to catalytic combustion principally at low temperatures. In 1819 Döbereiner discovered the tremendous activity of spongy platinum and developed his lamp for producing fire.[1] Dulong and Thenard found that other metals could be made to act in the same way as platinum and pal-

[1] Döbereiner, *J. Chem. Physik* 34, 91 (1822); 38, 321 (1823); 39, 159 (1823); 42, 60-4 (1824); 63, 465 (1831); *Gilb. Ann.* 74, 264 (1823).

ladium and that such materials as charcoal, pumice, porcelain, and glass become active at temperatures above 350° C.[2] Henry made his discoveries on preferential combustion.[3] Faraday studied the effect of diluent gases in retarding combustion at active surfaces.[4] The period ended with the controversy between Faraday and De la Rive in 1834-5 on the mechanism of such catalytic combustion as had been observed, Faraday expounding the theory of condensation at the catalyst surface and De la Rive holding the view that a series of rapidly alternating oxidations and reductions occurred.[5]

The suddenly stimulated interest in the subject gradually subsided and during the following fifty years, from 1836 to 1887, no major researches were conducted. In the latter year, however, Fletcher [6] presented an experimental lecture at the Manchester Technical School on "Some Curious Flames," during which he demonstrated a case of flameless surface combustion at the surface of iron wire. A bundle of iron wire first heated in a flame continued to glow red hot when the gas stream was momentarily interrupted and then continued. This demonstration was the first instance in which the conditions for the maintenance of high temperature surface combustion were shown. Fletcher conceived of the intensification of the combustion at surfaces, which Davy had not thought of, and explained that greater heat (presumably higher temperatures) was obtainable. However, he did not develop this idea any further and the influence of his experimentation and exposition was slight.

From 1902 on, however, the subject of surface combustion has been carefully investigated principally by Bone and his co-workers in England [7] and independently by Schnabel [8] in Germany. The early work of Lucke in this country, Bone and his co-workers in England, and Schnabel in Germany, has been followed by a technical development which will be discussed in more detail later.

The results of the early experimentation of Bone's work have led him to the formulation of certain general ideas regarding the phenomena. These may be briefly summarized as follows:

1. All surfaces possess the power to accelerate gaseous combustion, to varying extents, at temperatures below the ignition point.

2. Catalyst activity increases with the temperature of the surface, at high temperatures the differences between surfaces become less, and at temperatures of incandescence all surfaces are practically equal in activity.

3. The catalytic effect of heated surfaces depends on adsorption of the

[2] Dulong and Thenard, *Ann. chim. phys.* 23, (II), 440 (1823); 24, 380 (1823); *Gilb. Ann.* 76, 83 (1824); *J. Chem. Physik* 40, 229 (1824).
[3] Henry, *Phil. Mag.* 65, 269 (1825).
[4] Faraday, *Phil. Trans.* 1834, (I), 55; *Pogg. Ann.* 33, 149 (1834), "Experimental Researches on Electricity." (1828).
[5] De la Rive, *Pogg. Ann.* 46, 489,492 (1839); 54, 386,397 (1841); *Ann. chim. phys.* 39, 328 (1828).
[6] Fletcher, *J. Gas. Lighting* 1, 168 (1887).
[7] *J. Roy. Soc. Arts* 62, 787,801,818 (1914); *see also* Bone and Townend, "Flame and Combustion in Gases," London, Longmans, Green & Co., Ltd., 1927.
[8] Schnabel, *Ber.* 46, 5 (1913).

combustible gas, and probably of oxygen, at the surface. As it is known that hot surfaces emit streams of electrons, it is probable that the surface becomes activated through ionization and that the adsorbed reacting gases are thus activated.

4. The catalyst becomes electrically charged during the process of surface combustion through this electronic interchange.

5. Surface combustion in porous masses is confined to thin layers.

6. At low temperatures the most effective catalysts are the platinum metals, iron oxide and nickel oxide.

Surface Action

The controversy over the mechanism of surface action during flameless combustion started with the argument between Faraday and De la Rive and has continued to the present without any generally accepted, clear cut theory having been brought forward. Several of the theories regarding points at issue have been supported with experimental evidence, however, and require attention.

The lack of interest in surface catalysis during period of 1836 to 1887 may in a large measure be attributed to the influence of Siemens,[9] who propounded the theory that contact with hot surfaces retarded combustion by promoting dissociation in the reacting gases. This theory was generally accepted for a generation and during that time it was believed that contact between combustible gases and hot surfaces should be avoided as far as possible. Siemens had concluded from the work of Deville and others on the dissociation of steam and carbon dioxide that hot surfaces would retard combustion by first hindering the rapid motion of the molecules and second by causing dissociation of the gases. While he was thus correct in believing that surfaces can promote dissociation he was unaware of the fact that by this action surfaces could promote the attainment of equilibrium.

The view upheld by Faraday and generally attributed to have originated with the Italian physicist Fusinieri (1825),[10] that the capacity of certain materials in promoting combustion is due to their power to condense or adsorb the combustible gas, has been generally supported by subsequent experimentation at low temperatures.

Bodenstein's researches on the rate of certain heterogeneous gas phase reactions redirected attention to the adsorption theory and also brought the diffusion factor to the attention of experimenters.[11] He observed that the rate of reaction

$$2H_2 + O_2 = 2H_2O$$
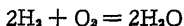
was very rapid at the surface of clean platinum even when the temperature of the metal was as low as $0°$ C., and that the rate was always propor-

[9] Siemens, *Proc. Roy. Inst.* **XI**, (1884-6), p. 471.
[10] *See* Bone and Townend, "Flame and Combustion in Gases," London, Longmans, Green & Co., Ltd., 1927, p. 33.
[11] Bodenstein, *Z. physik Chem.* **29**, 665-99 (1899); **46**, 625-76 (1903); **53**, 166 (1905); **60**, 1-45 (1907).

tional to the pressure of the $2H_2 + O_2$ mixture. When either hydrogen or oxygen was present in excess the rate was still proportional to the partial pressure of the $2H_2 + O_2$ mixture present in the gas. The results were explained by Nernst's diffusion theory,[12] which showed that when it is assumed that the rate of reaction at the active surface is infinitely rapid, the observed rate of reaction depends upon the rate of solution of the reacting gases in the adsorbed water film on the surface. When the temperature of the platinum surface is maintained at a temperature sufficiently high to prevent condensation of a water film, the rate of the reaction is very much increased and no longer follows the course of a first order reaction. In the oxidation of sulfur dioxide to sulfur trioxide at platinum surfaces in the temperature range of 150° to 250° C. the rate of combination is found to be proportional to the SO_2 concentration, independent of the oxygen concentration, and inversely proportional to the square root of the SO_3 concentration. This result again shows that when the actual rate of combination is considered infinite at the surface of the active material, the rate of diffusion of the reactants controls the rate of the observed reaction. It also shows that the rate of diffusion of the slower moving constituent, the SO_2 in this case controls the actual rate.

It thus came to be recognized that the rate of catalytic reactions could be governed by a variety of factors depending on the conditions. These factors may be itemized as: (1) the rate at which the reacting gaseous molecules can move up to and penetrate the film at the catalyst surface, (2) the rate at which either one or all of the reactants become active at the surface of the catalyst, (3) the actual rate of combination of the molecules, and (4) the rate at which the product or products can move away from or diffuse from the catalyst surface. The slowest rate will, of course, control the rate of observed reaction and the order of the reaction will be governed thereby. In general, and particularly where the reaction temperatures are moderate, diffusion rates will control the velocity of actual combination. In surface combustion, however, where the "catalyst" is hot enough to emit light rays, diffusion rates generally do not control, the vital factor in such cases being the "activation" of the molecules.

As a result of previous work with hydrogen and oxygen mixtures Bone and Wheeler [18] reached the early conclusion that true surface combustion depended upon one or both of the reacting gases becoming "activated" by contact with the hot surface. At that time they pointed out also that dissociation of the hydrogen atoms probably played an important part in the phenomena and pointed to the influence of hydrogen on the electron emissivity from hot metals. Ideas as to what constituted "activation," however, were not clear, and no distinguishing mark aside from increased reactivity was put on "activated" molecules.

[12] Nernst, *Z. physik. Chem.* 47, 52 (1904).
[13] Bone and Wheeler, *Phil. Trans. Roy. Soc.* 206A, 1-75 (1906).

"Activation" is today looked upon as the acquisition of a certain excess of energy by normal molecules, and is a perfectly general process applicable to both homogeneous and heterogeneous reactions. Before reaction can occur in either of these classes it is essential that some molecules be in a certain exceptional state wherein they react immediately or upon collision. In chemical reactions having measurable rates it has been shown that a small per cent only of actual collisions are effective in causing reaction, such effective collisions being between the active molecules, although all of the active molecules do not react as a result of "activation." Arrhenius showed that the velocity constant of a reaction may be expressed as a function of temperature by the relation:

$$\frac{d \ln K}{dT} = \frac{A}{RT^2}$$

where A is the energy of activation,[14] i.e., heat of formation of active molecules from normal molecules. This may be regarded as a chemical basis of activation. Although this general idea has been retained, modern interpretation puts activation on a more physical than chemical basis.

The mode of "activation" or of giving this exceptionally high energy content to favored molecules, particularly in such catalytic reactions as surface combustion, has been a controversial subject up to the present. Likewise, the concept of an "activated" molecule, or of what constitutes the exceptional energy, whether kinetic or internal,[15] requires further investigation before it can be used with assurance in explaining certain phenomena. In summation, it may be said that while adsorption of one or both of the reacting gases at the catalyst surface [16] followed by "activation" and reaction is a generally accepted explanation of surface catalysis, the mode of activation whether by ionization as proposed by Sir J. J. Thompson, by deformation of reacting molecules as recently advanced by Taylor,[17] by dissociation, or by some other phenomenon is still in doubt.*

The actual mechanism by which the surface, so called, of a substance like silica or alundum acts in the phenomena of "surface combustion" has not been demonstrated.[18] Many of the expositions on the subject have developed theories based on effects noted in low temperature combustions, where without doubt certain materials are selective in their action presumably through a process of adsorption. Whether such theoretical jumping from low temperatures to temperatures of incandescence, often as high as 1800° C., is justified has not been demonstrated by strong ex-

[14] Arrhenius, *Z. physik. Chem.* 4, 226 (1889).
[15] Langmuir, *J. Am. Chem. Soc.* 42, 2190-2205 (1920).
[16] *Compare* Rodebush and Nichols, *J. Am. Chem. Soc.* 52, 3866 (1930).
[17] Taylor, *Proc. Roy. Soc.* 113A, 77, 78 (1926).
* The reader is referred for further details regarding kinetics of reaction to such works as: a. Hinshelwood, "The Kinetics of Chemical Change in Gaseous Systems," Oxford, Clarendon Press, 1926; b. Bone and Townend, *loc. cit.;* c. Van't Hoff, "Studies in Chemical Dynamics," Easton, Pa., Chemical Publishing Co., 1896; "Lectures on Theoretical and Physical Chemistry," Eng. ed., 1898; d. Rice, "The Mechanism of Homogeneous Organic Reactions," New York, Chemical Catalog Co., Inc., 1928, A.C.S. Monograph No. 39.
[18] *See* Gibbs, *J. Soc. Chem. Ind.* 48, 127 (1929).

perimental evidence. Indeed, the fact that all surfaces apparently have the power to produce the effects of confined, flameless combustion when at high temperatures, seems to point to some stronger effect which hides the distinguishing features of catalysis noted at low temperatures and gives to all surfaces the same characteristics at incandescence.

Large surfaces will ignite inflammable gas mixtures at a lower temperature than small ones. With surfaces having an interstitial structure the temperature required for ignition may be much higher than for a surface of the same overall dimensions but of smooth structure.[19] All of the common solids having high melting points ignite mixtures of natural gas and air with about equal facility except in those cases where heat insulating films of scale or ash may form. Surfaces must be red hot to ignite mine gas mixtures and small surfaces as fine wires must be white hot.

Actually, it is difficult to see why catalysis, as it is thought of in low or moderate temperature work or with non-explosive mixtures should be a necessary factor at all in causing rapid reaction in explosive mixtures between oxygen and combustible gases at temperatures of 1400 to 1600° C.[20] An explosive mixture would be ignited instantly at such a temperature, i.e., the reaction between oxygen and combustible would proceed at a high rate, without the necessity for any catalytic intervention, due simply to the high *average* energy content of the molecules concerned. "Catalytic" reactions presume combustion in layers molecular in thickness at the catalyst surface since they depend upon the diffusion of molecules up to and formation on the active surface of monomolecular layers of either oxygen, combustible or both before reaction and yet it is improbable that at the temperatures observed in the hot porous masses all of the reaction occurs in such molecular layers.

When either metals or refractory oxides or silicates are used as catalysts for oxidation reactions in the gas phase, the speed of the reaction becomes very high when the surface becomes incandescent. Whatever the influence of any particular solid might be at temperatures below that necessary for, the emission of visible light rays, as the temperature approaches and surpasses that necessary for luminescence the effect of any solid becomes more and more equal to that of any other. This apparently anomalous behavior at high temperatures is probably due to the fact that an effect entirely different from that noted in low temperature work is overshadowing the specific effect of surface composition, namely, light catalysis.[21] The projection of an inflammable and intimate mixture of air and gaseous fuel on a highly incandescent surface subjects the mixture to the ionizing influence of the light energy, issuing from the hot surface. This effect combined with the very high temperature so increases the rate

[19] Guest, *U. S. Bur. Mines Tech. Paper* No. 475, 59 pp. (1930).
[20] *Compare* Gray, *J. Gas Lighting*, 126, 786-9 (1914).
[21] a. Blake, Chapter on "Surface Combustion" in "American Fuels," Vol. II, Bacon and Hamor, New York, McGraw-Hill Book Co., Inc., 1922; b. Rideal and Taylor, "Catalysis in Theory and Practice," London, Macmillan Co., 1919, pp. 410-36; c. Lewis and McKeown, *J. Am. Chem. Soc.* 43, 1288-96 (1921); d. Langmuir, *ibid.* 42, 2190 (1920).

of reaction that combustion is practically immediate, with the result that no flame is visible.

Retardation of Flame Propagation

Free and uncatalyzed flame in gaseous mixtures can occur either with (1) a slow, uniform motion, (2) an accelerating, vibratory motion, or (3) an exceedingly rapid explosion wave. The relatively slow, uniformly moving flame is of greatest importance in ordinary combustion work and is markedly influenced in speed by the shape and dimensions of the container in which it is being propagated. Flames of coal gas and air in any proportion cannot propagate in tubes of 2 mm. (0.08 inch) diameter or smaller, and with methane the limit is 3.6 mm. (0.142 inch).[22] However, propagation of a hydrogen flame has been reported to occur through a 0.9 mm. (0.035 inch) tube.[23] Through a one inch diameter tube the speed and composition of maximum speed mixtures are as shown by Table XX.

TABLE XX.—*Maximum Speed of Uniform Movement of Flame.*[24]

Gas	Max. Speed of Uniform Movement of Flame ft./sec.	cm./sec.	Combustible Gas in Air Per Cent
Hydrogen [a]	15.9	484.6	38.5
Carbon monoxide [b]	4.1	125	50.0
Hydrogen, carbon monoxide equal volume [b]	10.3	314	44.0
Coal gas [c]	5.2	158.5	17.0
Producer gas [c]	2.4	73	51.0
Pentane [c]	2.7	82	2.9
Acetylene [d]	9.35	285	9.5

The maximum observed and calculated flame temperatures and maximum speeds of uniform horizontal movement in 25 mm. tubes of flames of various hydrocarbon gases in air are shown in Table XXI.[25] These values of flame speed were compiled from the reports of Wheeler, Payman, Coward, and others by the U. S. Bureau of Mines.

Detonation, representing a very rapid method of combustion, is the propagation of a chemical reaction in a gaseous medium at a very high rate without the intervention of solid surfaces. The chemical change is propagated through the explosive mixture as an explosion wave by adiabatic compression and the heat generated in the reaction. The speed of such flame movement ranges from 6500 to 10,000 feet per second,[26] and is markedly suppressed by screens, porous bodies, and surfaces in general.

Thus, it may be seen that in all cases of flame propagation, the rate of movement of the flame front is quite finite even in the case of detona-

[22] Payman and Wheeler, *Fuel* 1, 185 (1922).
[23] Mallard and Le Chatelier, *Ann. Mines* (VIII), 4, 274 (1883).
[24] a. Georgeson and Hartwell, *J. Chem. Soc.* 1927, 265; b. Payman, *ibid.* 115, 1446, 1454 (1919); c. Haslam and Russell, "Fuels and Their Combustion." New York, McGraw-Hill Book Co., Inc., 1926; d. Mason and Wheeler, *J. Chem. Soc.* 115, 578 (1919).
[25] Jones, Lewis, Friauf, and Perrott, *J. Am. Chem. Soc.* 53, 869-83 (1931).
[26] Dixon, *Phil. Trans.* 184, 97 (1893).

TABLE XXI.—*Composition of Air-Hydrocarbon Gas Mixtures to Give Maximum Flame Temperatures, Maximum Speeds of Uniform Movement of Flame, and Complete Combustion.*[25]

Hydrocarbon	Obs. Max. Flame Temp.	Combustible in Air at Max. Flame Temp.	Combustible in Air for Complete Combustion	Max. Speed of Uniform Movement of Flame		Combustible in Air at Max. Speed of Uniform Movement of Flame	Calcd. Max. Flame Temp.
	° C.	Per Cent	Per Cent	ft./sec.	cm./sec.	Per Cent	° C.
Ethylene	1975	6.65–7.00	6.50	5.42	165	7.30–7.70	2072
Propylene	1935	4.45–4.90	4.45	3.28	100	5.00–5.40	2050
Butylene	1930	3.35–3.45	3.35	3.18	97	3.90–4.10	2033
Propane	1925	4.05–4.30	4.00	2.69	82	4.60–4.80	1967
Isobutane	1900	3.15–3.25	3.10			} 3.60–3.80 }	1973
Butane	1895	3.15–3.40	3.10	2.72	83		
Ethane	1895	5.70–5.95	5.65	2.82	86	6.30–6.60	1949
Pittsburgh natural gas	1890	8.60–9.10	8.60	2.33	71	9.10–9.40	1928
Methane	1880	9.45–10.10	9.45	2.2	67	9.70–10.00	1918

tions, and is markedly dampened by passage through small openings. It is, hence, conceivable by the proper use of gas composition, gas feed rates, and combustion spaces, that the flame front in either of the three types of combustion could be held stationary in a moving stream of combustible mixture rather than allowed to move through a relatively stationary gas mixture. This, of course, is what happens in ordinary combustion of gaseous fuels.[27] With explosive mixtures, however, burning at high temperatures and very high rates of flame propagation very high gas rates would be needed to keep the explosion wave "floating" in one position unless special means were available to prevent "back firing." By proper screening or baffling and removal of heat at the high temperature as fast as generated it should be possible to localize this exceedingly rapid chemical reaction. This is the view on which Lucke has based his developments.

This interesting viewpoint, which affords relief from the theories of surface action, was taken by Lucke in his early development of what was virtually the first surface combustion process.[28] In contrast to the other workers in the field, Lucke did not approach the problem from the viewpoint of catalytic action, but from the viewpoint of holding the flame of an explosive mixture stationary.[29] He recognized that it is desirable to obtain complete combustion without excess air or oxygen, and pointed to the utility of being able to burn an explosive mixture continuously and non-

[27] *Compare* Stevens, *Ind. Eng. Chem.* **20**, 1018-26 (1928).

[28] a. Lucke, Doctor's Dissertation at Columbia University (1900) presented as "The Heat Engine Problem" before the Am. Soc. Mech. Eng. in December 1901; *Cf. also* b. Editorial, *Ind. Eng. Chem.* **4**, 77-9 (1912); c. Editorial, *Power*, Nov. 12, 1911; d. Blake, chapter on "Surface Combustion," Bacon and Hamor, "American Fuels," New York, McGraw-Hill Book Co., Inc., 1922, Vol. II; e. Lucke, *Ind. Eng. Chem.* **5**, 801-24 (1913); f. Hutton, "The Gas Engine," New York, John Wiley & Sons, Inc., 1903, 1st Ed., p. 422-30.

[29] *See* Read, *Power* **45**, 225-6 (1917) also in this regard.

explosively under commercial conditions. If the rate at which an explosive mixture is fed is greater than the rate of flame propagation in such a mixture, the flame would "blow off," and if the reverse were true, i.e., flame propagation rate greater than gas velocity the flame would flash back. Lucke's problem was to adjust conditions so that neither of these undesirable events occurred and that rapid combustion of an explosive mixture took place in a localized zone. The process must be so conducted that the surface of combustion or "flame cap" could not move but remained localized for a variety of gas rates and mixtures as well as for different temperatures. In any case, the velocity of feed gas must be greater than the rate of flame propagation at some point before the surface of combustion is reached or else the flame would gradually work back and an explosion occur in the mixing chamber.

The only way in which these desirable features could be obtained was to feed the explosive gaseous mixture through relatively long, narrow orifices into a mass of broken refractory, and to allow the heat of the combustion to maintain the pieces of refractory at incandescent temperatures and thus localize the reaction at this high temperature zone. Proper adjustment of feed rates prevented back firing and the use of proper sized orifices relative to feed rates allowed of a certain degree of variation in heat output or attained temperatures. Lucke recognized the industrial significance of his success and patented his devices not only for combustible gases but for liquid fuels as well.[30]

Mechanism of Oxidation

When hydrocarbon fuels are being burned, the question of oxidation mechanism is also to be considered. The process of hydroxylation, which of necessity is stepwise and hence, relatively slow, probably is involved only to the extent to which time is allowed for oxygen to enter the hydrocarbon molecule as the gases are approaching the hot zone and are becoming heated. A catalyzed hydroxylation mechanism would also mean a succession of molecular trips to the "catalyst" surface before complete combustion of the hydrocarbon had occurred.

For methane, the simplest hydrocarbon, the hydroxylation mechanism is represented by the following equations which involve a possibility of several oxidation and decomposition steps.

$$CH_4 \xrightarrow{\frac{1}{2}O_2} CH_3OH \xrightarrow{\frac{1}{2}O_2} H_2CO \xrightarrow{\frac{1}{2}O_2} CO + H_2O \xrightarrow{\frac{1}{2}O_2} CO_2 + H_2O$$

$$CH_3OH \downarrow$$
$$CO + 2H_2 \qquad CO + H_2$$
$$1\frac{1}{2}O_2 \downarrow \qquad \downarrow O_2$$
$$CO_2 + 2H_2O \qquad CO_2 + H_2O$$
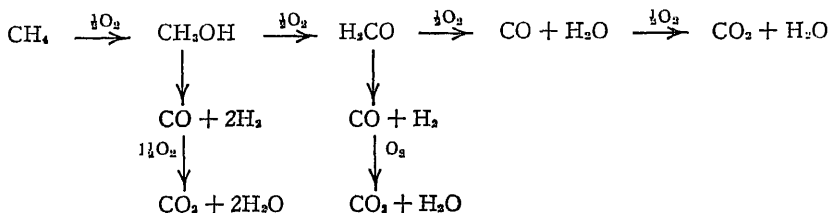
[30] Lucke, U.S. Pat. 755,376 filed June 7, 1901, and U.S. Pat. 755,377 filed July 30, 1901; issued March 22, 1904.

At the temperatures of the porous masses obtained in practice dissociation of hydrocarbons as are present in commercial gases is thermodynamically complete, and interaction between oxygen and the active hydrogen and carbon thus released must be very rapid and complete. It is reported, however, that methane is not completely decomposed at 1300° C. at the end of an hour according to the reaction:

$$CH_4 = C + 2H_2.$$

Ethane, being less stable than methane, can be decomposed very rapidly by heating to 1150° C.[24] For the higher hydrocarbons, Katz,[31] has estimated that 0.036 seconds are required for complete decomposition at 1500° C. At temperatures of 1800° C. and in the presence of incandescent solids emitting large quantities of light energy decomposition of all hydrocarbons would be very much more rapid. Depending upon conditions which will determine the relative rates of the processes involved, thermal or photo-decomposition and hydroxylation may compete although in the majority of instances of surface combustion, dissociation followed by oxidation should prevail.

Industrial Application

The complete and continuous burning of explosive mixtures of combustible and air, usually in theoretical proportions, without flame and in contact with an incandescent solid has several claimed advantages. These may be enumerated as: (1) combustion is very rapid and is localized, (2) combustion is complete without the use of excess air, (3) very high temperatures can be obtained without the necessity for preheating the feed gases and, (4) the developed heat is transferred very rapidly, largely by radiation.

The application of the principles of surface combustion has resulted in the development of four general types of apparatus. These forms may be described as (1) the diaphragm adaptation in which the explosive mixture burns in a porous block of refractory, Figure 21, (2) the granular bed type as used in crucible furnaces and boilers, shown in Figure 22, (3) a similar type but utilizing a high velocity gas stream directed against a bed of broken refractory, Figure 26, and (4) the arch or tunnel type of burner in which the burning gas mixture plays over a refractory wall, Figure 28.

Diaphragm type. The diaphragm form of apparatus consists of a block of porous refractory through which the gaseous combustible mixture is forced. After ignition of the mixture at the front face, the surface of the refractory becomes hot, the flame becomes smaller, and soon all combustion occurs within the pores of the block near the surface, if conditions are properly controlled. Due to the complete and intimate mixing that has taken place between the combustible and the air, and to the extreme

[31] Katz, *U.S. Bur. Mines Tech. Paper* No. 183 (1918).

rapidity of the combustion no flame appears and combustion is complete in a very small zone. This form of apparatus has found application in the evaporation or concentration of liquids and in certain cooking operations as grilling, roasting, etc. Heat may be radiated to any body at a lower temperature than the face of the block from any position since the apparatus may be inverted, or pointed in any direction, or made in curved, special shapes.

Several difficulties have been encountered in the use of this form of apparatus, the most easily solved of which has probably been the clogging of the pores by foreign matter in the ingoing gas mixture. The necessity of freeing the gases from dirt and dust particles is obvious and the use of such clean gas mixtures has eliminated the difficulty.
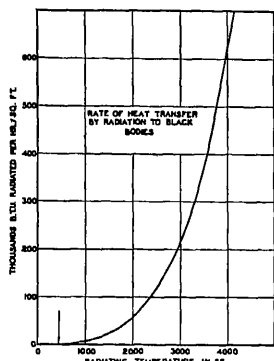
FIG. 20.—Heat transfer by radiation.
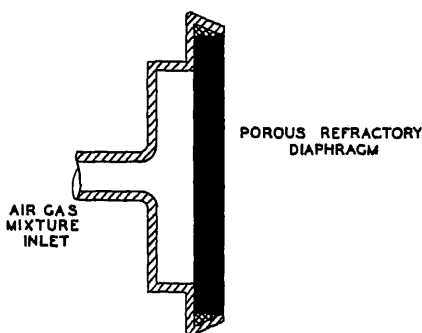
FIG. 21.—Porous diaphragm surface combustion apparatus.

The chief limitation, however, of the diaphragms as they were originally used was that if free radiation from the outward surface was impeded, the refractory layer in which combustion was occurring would become so hot as to heat the next layer behind it to a temperature at which it could induce combustion. The seat of rapid combustion would thus move inward and in time reach the back face of the porous block which would become hot enough to detonate the incoming explosive mixture of gases. This difficulty greatly retarded the development of surface combustion in this form of apparatus, and required considerable experimentation for its successful solution. This limitation has been overcome by the use of different sized granules increasing in size from very small at the front to larger ones at the back of the porous block. It is even claimed that two of the newer diaphragms in operation may be placed face to face without danger of back popping.[32]

The necessity of using both air and gas under pressure, air usually at about 4 in. water pressure and gas at about 3 ins., has retarded the

[32] Brit. Pat. 245,182 (1924) Cox.

application of this form of apparatus to more universal domestic use. The necessity for having the air under pressure makes the installation of a motor blower or some other source of compressed air imperative. Industrially this factor has not been significant since air under pressure is usually available or can be made so at small inconvenience or cost.
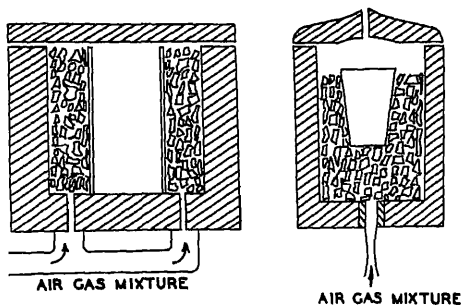
FIG. 22.—Surface combustion crucible furnaces.

The working life of these porous diaphragms is satisfactory, the early ones having shown a life of over four years without noticeable deterioration while operating 9 hours a day excepting holidays.[33] Cleaning is easily accomplished when necessary by washing with water.

Refractory bed type. The second, and generally more important form of apparatus is that shown in Figure 22, which utilizes a bed of broken refractory granules. In this form, the combustion occurs in the bed of granules which is maintained at incandescence. Using gas of
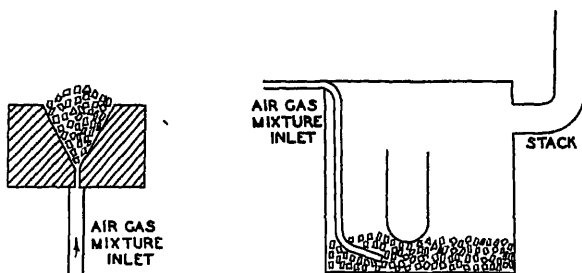
FIG. 23.—Early forms of surface combustion apparatus.

600-700 B.t.u. per cu. ft. heating value properly mixed with air very high temperatures are attainable, limited chiefly by the melting point of the refractory. With a furnace of the type shown it has been possible to fuse platinum foils (m. p. 1755° C.) in the crucible. The temperature of the refractory granules themselves is somewhat higher than this even.

Many modifications of this type of apparatus have been developed for

[33] Tulloch, *J. Soc. Chem. Ind.* **45**, 282T (1926).

different purposes. The two early forms designed and patented by Lucke [28] shown in Figure 23, foreshadowed many of the later forms as may be seen by a comparison of the figures. To properly distribute the gaseous mixture and prevent back flashing of the flame, Lucke [34] pierced the base of the burner with a large number of fine holes as in the domestic burner, Figure 24. With a burner of this type it was possible to burn completely and without excess air 2460 cu. ft. of 600 B.t.u. gas per hour per sq. ft. of bed or to generate nearly a million and a half B.t.u. per sq. ft. of surface per hour.[35]
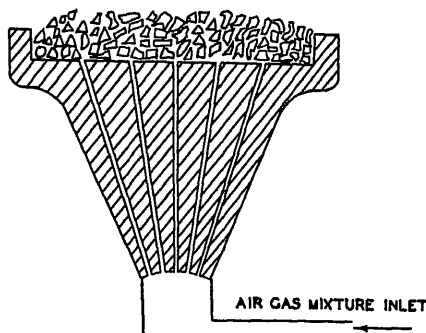
FIG. 24.—Type of burner proposed by Lucke for use in domestic cooking.

One of the more important forms that this development has taken, however, is in the generation of steam. In this application a modified fire tube type of boiler has been used in principle, but instead of having flames passing through the tubes they are filled with broken refractory granules which become incandescent by the heat generated at their surface in the intense combustion of an explosive mixture. This form of boiler shown in Figure 25 consists essentially of a series of tubes packed with broken refractory and immersed
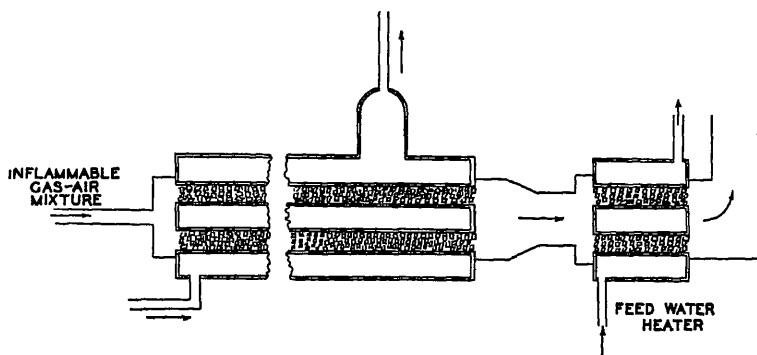
FIG. 25.—Surface combustion boiler.

in water. Air and gas are admitted to a small free space at one end of the tubes from suitable headers and are here mixed prior to entering the refractory bed. Combustion is rapid and practically complete at or about the entrances of the tubes, and the remainder of each tube serves for the abstraction of the sensible heat of the combustion products by the water.

[34] Lucke, *Ind. Eng. Chem.* 5, 801-24 (1913).
[35] For modifications *compare Tech. moderne* 19, 72-4 (1927).

Any heat still remaining in the exit gases from the boiler may be used to preheat feed water by passing the gases through similarly packed tubes immersed in the water.

With a single steel tube 3 ft. in length and 3 in. in diameter packed with fragments of granular refractory material, it was possible to burn completely a mixture of 100 cu. ft. coal-gas plus 550 cu. ft. air per hour and to obtain an evaporation of 20 to 22 lbs. of water per sq. ft. of heating surface when the exit combustion gases were at a temperature of practically 200° C. Combustion was completed within 4 or 5 inches of the point where the gases entered the tube and a thermal efficiency of 88 per cent was realized. Evaporation was distributed as follows along the length of the tube, 70 per cent over the first third of the length, 22 per cent over the next third, and only 8 per cent over the last third, and shows the effectiveness of heat transfer from combustion zone to the water. The highest temperature of 1400° C. occurred at a distance of about 1 ft. from the inlet end.* The last two-thirds of the tube serves to abstract the heat rapidly from the combustion products by forcing them to move at high velocity against the tube wall and the refractory granules and thus to minimize the gas film on these surfaces which ordinarily reduces heat transfer. The high exit gas temperature in this test prevented higher thermal efficiency from being shown.

Industrial scale boilers of the *Bonecourt* type developed by Bone and McCourt[36] have had successful operation. A 110-tube boiler with tubes four feet long and 3 in. internal diameter packed with fragments of refractory granular material has been operated on washed coke oven gas with an efficiency of 92.7 per cent and a rate of evaporation of 14.1 lbs. steam "from and at 212° F." per sq. ft. of heating surface per hour. This compares with an efficiency of 75.1 per cent and an evaporation of 4.3 lbs. steam per sq. ft. heating surface per hour for a coal fired marine boiler. In operation, the combustible gas with the regulated amount of air is drawn under suction from a fan, through the boiler tubes where it is burned completely and then through packed tubes in the waste heat feed water heater where the temperature of the stack gases is lowered to about 80° C.

Boilers fitted with 38 tubes 15 ft. long and 6 in. diameter have been successfully operated. The tubes in these boilers were packed with a rigid system of refractory blocks on which surface combustion occurred rather than with the broken refractory granules since practice had shown the granules to be unsatisfactory when operated with such dirty gases as producer gas. Very flexible and efficient operation resulted from use of these boilers.**

Numerous advantages are claimed for surface combustion boilers. Some of these may be enumerated as: (1) The boilers are very compact and free from elaborate brick work settings. (2) Forced firing can never

* *See* Ref. 36, p. 460.
[36] Bone. "Coal and its Scientific Uses," London, Longmans Green Co., 1922, p. 458 *et seq.*
** *See Ref.* 36, p. 468.

overheat the boiler shell since all combustion occurs in the tubes under the water surface. (3) Good circulation of water is induced by the steep evaporation gradient from front to back of the boiler. (4) The operation is extremely flexible since only as many of the tubes as are necessary need be used. (5) High efficiencies may be realized. However, gaseous or liquid fuels are necessary and impose a severe handicap on the system.

Several difficulties relative to the application of surface combustion in gas-fired steam boilers have been pointed out.[87] The molecular strain caused by the intense heat in the metal tubes is certain to weaken the metal. The localization of heat gives a tendency to priming which, however, may be avoided by inclining the tubes or by having them vertical. Where coal has to be gasified first the losses in the gasification process may offset the very high efficiencies attainable in the boiler.
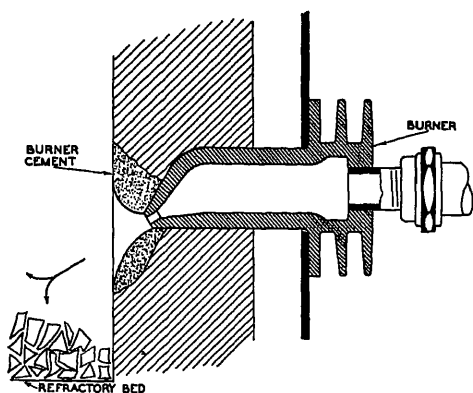
Fig. 26.—Refractory bed type of furnace. (Surface Combustion Co.)

High velocity gas stream impinging on refractory bed. If a jet of an inflammable gas mixture moving at a high velocity is allowed to impinge on a bed of broken refractory material and ignited, the velocity is sufficiently reduced by the refractory to permit combustion to occur at or near the surface of the bed. Then if radiation to a cold surface is not too rapid the hot part of the refractory may assume a temperature close to the theoretical flame temperature. When theoretical air-combustible mixtures are used, the combustion is so complete in the refractory bed that a non-oxidizing atmosphere consisting of nitrogen, carbon dioxide, and water vapor exists at a very short distance from the bed. The advantage of radiant heat utilization, small combustion zone, non-oxidizing atmosphere, complete combustion, etc., have made this type of surface combustion furnace valuable to a number of industrial processes.

Figure 26 shows the refractory bed type of firing with the burner in place to project the inflammable mixture against the bed of refractory

[87] Latta, *Am. Gas Light. J.* 105, 225-9 (1916).

material. The velocity of gaseous mixture leaving the burner nozzle must be greater than the rate of flame propagation to prevent back firing into the proportioning apparatus. The minimum velocity allowable varies with the different gases used because of the different rates of flame propagation. Any material may be used for the bed provided it will stand a
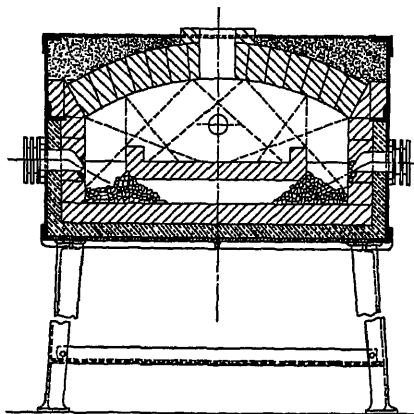
Fig. 27.—Surface combustion furnace.
(Surface Combustion Co.)
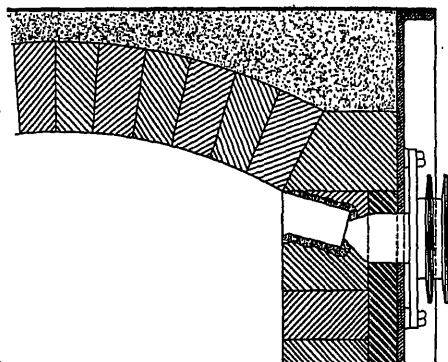
Fig. 28.—Arch type of furnace.
(Surface Combustion Co.)

temperature of about 3400° F. (1871° C.). In small installations the burner nozzles are cooled by radiation from metal fins provided near the inlet. On large installations water cooling must be resorted to in order to prevent premature combustion and explosions in the nozzle.

A furnace designed to give uniform temperature distribution across
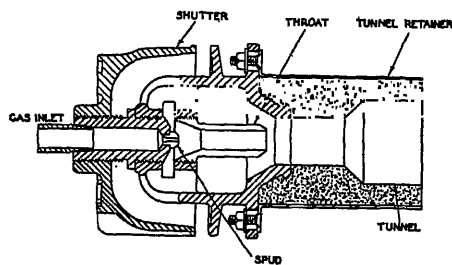
Fig. 29. (Surface Combustion Co.)

the width by radiation from the arched roof is shown in Figure 27. Such a furnace is valuable in the heat treating of metals where oxidizing conditions must be avoided and uniform heating assured.

Tunnel type. The tunnel or arch type of burner is shown in Figure 28. It consists of an accurately designed combustion chamber lined with a cement capable of withstanding over 3400° F. In this type of construc-

tion the entering gas mixture is projected at a high velocity along the refractory arch at the surface of which combustion occurs at a high rate. The arch is so designed that combustion of the gases is complete before
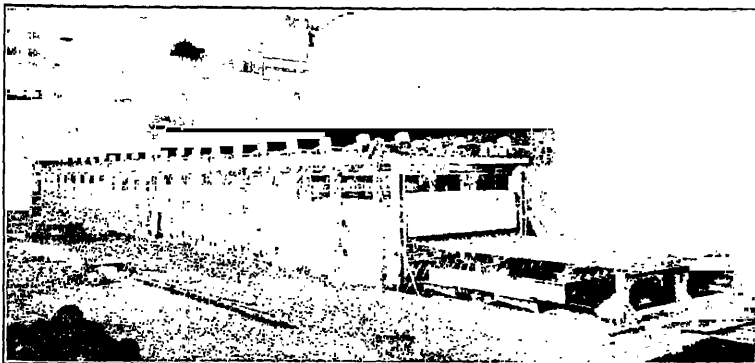
FIG. 30.—Surface combustion sheet normalizer. (Surface Combustion Co.)

the end of travel along the surface. Heat is transferred to the object in the furnace by radiation from the roof.

Mixing Devices

For proper operation of surface combustion devices it is essential that rapid and intimate mixing of air and gas in the correct proportions be
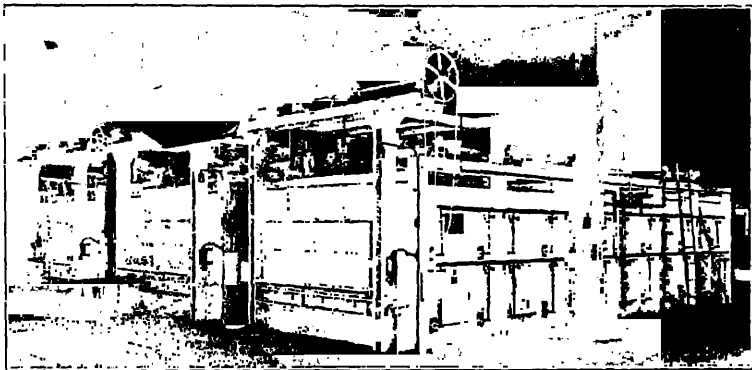
FIG. 31.—Surface combustion pack heater. (Surface Combustion Co.)

maintained constantly during use. This is accomplished by automatic proportioners or inspirators, one form of which is shown in Figure 29. These devices operate on the Venturi meter principle and use the velocity head of one of the constituents to draw in or inspirate the other. They are so designed that the correct proportion of air to gas is maintained

constant regardless of feed rate. Single inspirators are now in use ranging in maximum capacities of 80 cu. ft. per hour to 20,000 cu. ft. of 1000 B.t.u. gas per hour.[38]

The proportioning systems and burners are so designed that pressures of about 0.5 inch of water may be used with coke oven gas high in hydrogen, or 0.2 inch water with natural gas having a lower rate of flame propagation.

The Incandescent Gas Mantle

Although the heating of a refractory material to incandescence for the purpose of a source of light had engaged the attention of a number of earlier experimenters, it was not until 1880-3 that Williams, in New Jersey and Welsbach in Vienna developed what is essentially the gas mantle of today.[39] Cotton threads impregnated with a solution of a rare earth salt, dried, and burned resulted in the formation of a coherent ash which emitted light of great intensity when heated by a gas flame.

Welsbach first patented thoria as the mantle material,[40] believing that it was possessed of high capacity for light emissivity. He later found that the brilliant luminosity of his early products was due to the presence of small amounts of ceria. The addition of about 1 per cent of ceria to the thoria used in making the mantles resulted in a mantle with over ten times the emissivity of those containing no ceria. Further addition of ceria, however, resulted in a progressive diminution of brilliance until when as much as 10 per cent had been added the luminosity was again small.

Various explanations for the phenomena have been advanced, the most probable of which is that based on catalytic action. The fact that other metallic oxides, which act as oxygen carriers and which could, hence, act as oxidation catalysts, such as vanadium pentoxide, manganese oxide, chromium oxide, uranium oxide, etc., have also been used for the purpose strengthens the idea that ceria acts as a catalyst for the combustion of the gas-air mixture at the mantle surface thereby concentrating the heat of reaction and raising the temperature of the thoria. Rideal and Taylor classify several of the oxides in the order of activity when used with a thoria base by noting the amounts required to obtain a given result. Thus, with 0.9 to 1.0 per cent of ceria as a basis for comparison, 0.4 per cent V_2O_5, 1.5 per cent of MnO_2, and 0.25 per cent U_3O_8 give equivalent results. Alumina has also been used as a base material in place of thoria, and beryllium salts are used in the impregnating solution to impart greater hardness to the finished article. Inert refractory material containing thoria and radioactive uranium oxide has been patented for the production of heat by catalytic combustion of gaseous fuels.[41]

[38] Personal communication, Surface Combustion Co., Toledo, Ohio.
[39] a. Rideal and Taylor, *loc. cit.*, p. 122; b. Green, "Industrial Catalysis," New York, Macmillan Co., 1928, p. 108.
[40] Welsbach, Ger. Pat. 41,945 (1886).
[41] U.S. Pat. 1,198,542 (1916) Harding.

A number of other materials has been found to be unsatisfactory for practical use, although applicable to demonstration or experimental purposes. Thus, the oxides of iron and cobalt, although catalytically active, are too volatile, as is magnesia when used as a base material. Calcium oxide is too readily attacked by water vapor and carbon dioxide of the air when cold to be practicable.

Why the activity of ceria is so critically restricted to the narrow zone of 0.9 to 1.0 per cent when used with thoria is not generally known. Meyer and Anschütz [42] have found that CeO_2 forms a solid solution with thoria up to 7 per cent and that in used mantles some CeO_3 is present. However, no experimental evidence has been produced to show that the maximum dissociation of ceria dissolved in thoria occurs at the critical range of about 1 per cent concentration.

[42] Meyer and Anschütz, *Ber.* **40**, 2639 (1907).

Chapter XI

The Cause and Suppression of Knocking in Internal Combustion Engines

Under certain conditions of operation the explosing occurring in automotive engine cylinders deviates from the normal and a high pitched, metallic note is audible. This sound is called a knock. It occurs particularly when the engine is accelerating from a low speed, is laboring on a hill, or is full of carbon. A large amount of investigation has been expended in attempts to determine the cause and remedy for this knock, but only such phases as border on catalytic effects, positive or negative, and which deal with the mechanism of the oxidation reaction will be considered here.

Since many factors such as nature of flame propagation, effect of radiant energy, effect of temperature and pressure, influence of turbulence, composition of fuel, etc., are operative, it is not surprising that no single, simple theory has been evolved which satisfactorily explains all the attending phenomena. Recent trends in the research on knock prevention have been concerned largely with the actual oxidation mechanism of single, pure hydrocarbons both in the presence of and without materials known to inhibit knock.

The hydrocarbons comprising modern motor fuels, paraffins, olefins, naphthenes, and aromatics, exhibit distinct class properties toward knocking and individual members of each of the groups show characteristic effects. The tendency to knock of the several groups may be classified as follows: [1]

1. The straight chain paraffins are very prone to knock. The branched chain isomerides have less tendency to knock and may even be good non-knocking fuels.

2. While the olefins have less tendency to knock than the paraffins they vary considerable in this respect depending on molecular structure.

3. Very little is known of the class properties of the naphthenes but in general they have less knocking tendency than the paraffins.

4. The aromatics are excellent non-knocking fuels and vary very little among individual members in this respect.

Alcohols show very little tendency to knock and the use of methanol as a motor-fuel blending material has received considerable publicity.

[1] Edgar, *J. Soc. Chem. Ind.* 47, 230-2T (1928).

At the present time resort is had to the addition of certain materials, known as antiknocks, to a knocking gasoline to suppress the tendency to detonate. Lead tetraethyl has found widespread use for this purpose and is effective in very low concentrations. Thus one part of lead tetraethyl by volume in 1300 parts of gasoline is equivalent in knock suppression to a 40-60 benzene-gasoline blend. In Europe metallic carbonyls, especially iron pentacarbonyl, have been used to some extent. However, they are not as effective as the lead compound and as their use is attended with certain difficulties, they have not been generally adopted as knock suppressers. The action of these materials in preventing knocking has been attributed to the breaking of "reaction chains" during the combustion, which ordinarily would have exceeded a certain critical velocity to cause a knock in the engine.

Recent investigations have disclosed that yet another factor has to be considered in the preparation of fuels for modern internal combustion engines, that of pre-ignition. Pre-ignition has been attributed to too early an ignition of the combustible charge by very hot particles of carbon or projections in the engine cylinder. The effect of this early ignition has been described as a knock but distinct in quality from the detonation knock. For economic and satisfactory engine operation it is hence necessary that this effect must be overcome.

OXIDATION MECHANISM

In the attempts that have been made to explain the action of certain compounds in suppressing the "knock" in internal combustion engines, it was early recognized that an understanding of the mechanism by which combustion occurred was essential to a successful solution of the problem. Consequently considerable experimental work and much speculation has been expended in the formulation of combustion mechanisms. A number of the earlier proposed theories have been largely discredited and more suitable ones substituted.

The Hydroxylation Theory

The hydroxylation theory of Bone[2] and his co-workers has had wide acceptance as far as the oxidation of aliphatic hydrocarbons is concerned. The mechanism postulated involves the successive formation of hydroxyl compounds, which may add oxygen to form additional hydroxyl groups or which may lose water and decompose. In this way methane would first form methanol, then methylene glycol which would be decomposed to formaldehyde and water; formaldehyde would be oxidized to formic acid or decomposed to carbon monoxide and hydrogen. The theory, however, is open to a number of criticisms.

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[2] a. Bone and Andrew, *J. Chem. Soc.*, **87**, 1232 (1905); b. Bone and Drugman, *ibid.* **89**, 660 (1906); c. Bone and Stockings, *ibid.* **85**, 693 (1904); d. Bone and Wheeler, *ibid.* **81**, 535 (1902); e. Bone and Wheeler, *ibid.*, **83**, 1074 (1903); f. Bone and Wheeler, *ibid.*, **85**, 1637 (1904); *compare* Chapter VI.

The products such as the mono- and di-hydroxy derivatives of the hydrocarbons, which are essential to the theory, have not been found experimentally except under special conditions where other factors are involved. An aldehyde and water have usually been the first products of oxidation to be observed.[3] The explanation offered by Bone and Stockings[2c] for the non-appearance of mono-hydroxy products in the experiments is that the primary alcohols undergo such rapid oxidation or decomposition that their presence in the product could not be expected. This is not in accord with the results of other workers who have found that in the case of paraffins higher than ethane the alcohols are more difficult to oxidize than the corresponding normal paraffins or normal aldehydes.[4] It has also been possible under certain circumstances, such as oxidation in the presence of nitrogen oxides, ozone, etc., to actually obtain the alcohol. It is difficult to see why, if the alcohol is so much more easily oxidized than the hydrocarbon, it would not be destroyed in these cases as well as in the process of direct oxidation where aldehydes but not alcohol have been found.

It has been shown that alcohols like benzene have ignition temperatures higher than corresponding normal paraffin hydrocarbons and that they are also excellent non-knocking fuels.

Another objection to the theory may be based on the experimental data existing on alcohol oxidation. According to Bone, alcohols should oxidize through a dihydroxy compound by the addition of an oxygen atom. The work of Wieland[5] and others has shown that the formation of aldehydes from primary alcohols may take place by dehydrogenation rather than further hydroxylation. Experimental evidence is lacking for the formation of the simple glycols by alcohol oxidation.

The necessity for the dissociation of the oxygen molecule into atoms in order to form the dihydroxy compound from alcohol has also met opposition. Such disruption of the oxygen molecule would probably be accompanied by ionization and yet there is no direct evidence that such occurs.[6, 4b]

Armstrong[7] using a mechanism similar to that of hydroxylation has considered the presence of water essential and formulated a mechanism in which oxygen and water acted as a unit to form dihydroxy derivatives of the hydrocarbons and hydrogen peroxide. The formation of the dihydroxy derivatives or of hydrogen peroxide was not shown. The validity of this theory has been questioned on the basis of the necessity for a trimolecular reaction and also on the basis of some work on the

[3] a. Wheeler and Blair, *J. Soc. Chem. Ind.* **42**, 81T, 419T (1923); b. Bone and Drugman, *J. Chem. Soc.* **89**, 660 (1906); c. Layng and Soukup, *Ind. Eng. Chem.* **20**, 1052 (1928); d. Howe, *Ind. Eng. Chem.* **20**, 342 (1928); e. Elworthy, *Trans. Roy. Soc. Can.* **16**, III, 93 (1922); f. Bone and Drugman, *Proc. Chem. Soc.* **20**, 127 (1904); g. Landa, Academy Science Paris, *Nature* **121**, 559 (1928).

[4] a. Layng and Youker, *Ind. Eng. Chem.* **20**, 1048 (1928); b. Callendar, *Engineering* **123**, 147 (1927).

[5] Wieland, *Ber.* **45**, 493 (1912); *cf. also* Chapters III and IV.

[6] Bennett and Mardles, *J. Chem. Soc.* **1927**, 3155.

[7] Armstrong, *J. Chem. Soc.* **83**, 1088 (1903).

oxidation of acetylene in the absence of water.[2a] Also, Stephens[8] concluded that alcohols were not intermediate in the oxidation of the aliphatic side chains of aromatic hydrocarbons and that the oxidation was similar to that in the case of aliphatic hydrocarbons. Water was found actually to retard the reaction. Stephens proposed a theory involving the formation of a complex between oxygen and the hydrocarbon, which subsequent to formation split to give water and an unsaturated residue. Rearrangement of the unsaturated residue resulted in the formation of aldehydes or ketones.

The steps in the oxidation subsequent to the formation of aldehydes are not so controversial. The aldehyde is generally decomposed or oxidized further to an acid or a lower aldehyde. The final products of oxidation are, of course, dependent upon several factors, such as temperature, catalysts, time, pressure, ratio of oxygen to fuel, etc.

Peroxidation Theory

Although considerable controversy has existed and still exists regarding the exact manner in which a hydrocarbon oxidizes, one fact stands out from the great mass of data that have accumulated and that is that aldehydes appear early and are prominent in the oxidation products. It has been recognized, however, that aldehydes are not the primary products of the encounter between oxygen and hydrocarbon molecules, and it has been proposed that the most probable initial product is peroxidic in type. While the protagonists of the hydroxylation theory concede the attractiveness of certain features of the peroxide theory, they consider that it does not contradict the evidence for the hydroxylation theory.[9]

In his work on the oxidation of saturated hydrocarbons with ozone, Harries[10] was led to propose the formation of a reactive peroxide. Although the experimental evidence for the formation of such a compound was meager, Harries accurately forecast the development of the theory. The exact nature of the peroxide formed in hydrocarbon oxidations has not been demonstrated and as a result the question is still under discussion. Whether the first or unstable peroxide, termed "moloxide" by Grün, Ulbrich, and Wirth,[11] that is formed decomposes as such, reacts with another hydrocarbon molecule, or is transformed into a more stable peroxide is uncertain.

The peroxide theory has developed largely from work in the liquid phase or at low temperatures conducted primarily in an attempt to solve some of the questions regarding knocking phenomena. It has been assumed that the evidence obtained in this manner would be directly applicable to the high temperature vapor phase oxidation. It has thus been assumed that the mechanism followed by the oxidation at relatively

[8] Stephens, *J. Am. Chem. Soc.* **50**, 2523 (1928).
[9] Bone, *Nature* **122**, 203-4 (1928).
[10] Harries, *Ann.* **343**, 311 (1905); **374**, 288 (1910); *see also* Chapter VI.
[11] Grün, Ulbrich, and Wirth, *Ber.* **53B**, 987 (1920).

low temperatures and at atmospheric or low pressure is the same as, or sufficiently similar to that at the high temperatures and higher pressures existing in an engine cylinder to make the results useful in interpreting engine operation. Also the evidence from combustion in perfectly homogeneously mixed gases and vapors has been applied in explanation of phenomena occurring during the combustion of extremely non-homogeneous mixtures as exist in engine cylinders.

The evidence in support of the peroxide theory lies mainly in the finding of very active forms of oxygen in the mixture during oxidation, although the tendency to form chain reactions and the inhibiting action of certain compounds are of considerable weight. These active forms of oxygen have been attributed to peroxides similar to those formed during aromatic aldehyde oxidation. Peroxides, as such, have not been isolated in aliphatic hydrocarbon oxidation processes but considerable evidence has been accumulated by a number of different workers to show their existence.

Pure benzaldehyde in an atmosphere of pure oxygen at 25° C. oxidizes slowly at first, passing through an induction period, then more rapidly, and finally attains a maximum rate of oxygen absorption. Treatments that serve to shorten the induction period increase the rate of oxygen absorption and *vice versa*. The addition of benzoyl peroxide increases the rate and the addition of benzoyl alcohol decreases it.[12] The period of induction has been supposed to correspond to the formation of peroxides which accumulate until the reaction undergoes autoxidation and the rate increases very rapidly. Similar phenomena have been observed with hydrocarbons.

The formation of peroxides was reported by Bach[13] in a study of the slow oxidation of mineral oil. Callendar[14] made extensive studies of the oxidation of hydrocarbons higher than hexane in supporting his theory of the cause and prevention of knocking. He found that aldehydes constituted 70 per cent of the products in the early stages of paraffin hydrocarbon oxidation. He obtained positive tests for peroxides and found that the amount of peroxide increased as the paraffin series was ascended from pentane to undecane. This finding lends support to the peroxide theory of knocking since the knocking tendency of the paraffin hydrocarbons increases with increase in molecular weight.

Mardles[15] passed hexane-air mixtures through hot tubes and reported the presence of active oxygen in the products. He supports the peroxide theory of combustion for this reason and because it offers a better explanation of engine knocking than does the hydroxylation theory. He has also proposed that the oxidation occurs in two steps, the first of which is peroxide formation followed by aldehyde formation through decomposition of the active molecule.

[12] Berl and Winnacker, *Z. physik. Chem.* 148A, 261-83 (1930).
[13] Bach, *Compt. rend.* 124, 951 (1897).
[14] Callendar, *Engineering* 121, 477 (1927).
[15] Mardles, *J. Chem. Soc.* 1928, 872-5.

Tests for active oxygen, with potassium iodide as a reagent, in the products from the autoxidation of petroleum fractions at 160° C. gave positive results indicating peroxides. Tests of the exhaust from running gasoline engines have also indicated the presence of peroxides.[16] It should be noted, however, that the potassium iodide-starch method shows the presence of hydrogen peroxide and that the tests reported may not have indicated the presence of organic peroxides for this reason. As a test for the presence of active oxygen the method is positive.

In the combustion of hydrocarbons, the effect of inhibitors, such as phenol or aniline, on the gaseous oxidation is similar to the effect on the oxidation of benzaldehyde in liquid form. The conclusion has been drawn that the mechanism of the oxidation in the two cases is the same. Egerton [17] believes that gaseous combustion should be interpreted according to the following steps: (1) The reaction will begin when a sufficiently active molecule of the fuel encounters an oxygen molecule having a high energy content, (2) a "temporary" peroxide is formed by this encounter and possesses a high energy value, (3) this peroxide breaks down to aldehyde and water. These products of the peroxide decomposition would possess the initial energy of activation as well as the energy of the reaction and would be in a favorable condition to react further with other oxygen or fuel molecules to start a chain of reactions. The conversion of "temporary" into a stable peroxide prior to further reaction or decomposition is also postulated. Evidence for the formation of the "temporary" peroxide, however, is not conclusive.

The fact that rapid or explosive reaction is preceded by a period of induction in the case of hydrocarbons as well as in the case of aromatic aldehyde oxidation favors the hypothesis that it is during this period that peroxides are forming and accumulating. When the concentration of peroxide reaches a critical value, chain propagation ensues, causing excitation and combustion of molecules coming into contact with the reaction centers of the chain.[18] In the case of hexane, peroxides to the extent of 3.2 per cent of the hydrocarbon have been shown to be present. The peroxide, once formed, can react either at such surfaces as may be present or in the gas phase. The period of induction is greatly affected by the oxygen concentration at constant temperature, by the presence of inhibitors such as aniline, or by the presence of surfaces. Reaction velocities are high during this period and the temperature coefficient is high.

Brunner [18, 19] studied the slow oxidation of a mixture containing 42 per cent hexane, 57 per cent oxygen and 1 per cent nitrogen at 210° C. with and without inhibitors present. Although reaction velocities are high at first as determined by analysis, the pressure change is slight. When aniline was present no reaction occurred at first, after which period

[16] a. Moureu, Dufraisse and Chaux, *Compt. rend.* 184, 413-7 (1927); *Ann. combustibles liquides* 2, 233-52 (1927). b. Dumanois, *Engineer,* May 8, 1931; *Fuel,* July, 1931, p. 292.
[17] Egerton, *Nature* 121, 10 (1928).
[18] Brunner and Rideal, *J. Chem. Soc. (London)* 1928, 1162-70.
[19] a. Brunner, *Helv. Chim. Acta* 11, 881-97 (1928); b. Brunner, *ibid.* 13, 197-207 (1930).

the normal induction reactions took place. Later the pressure increased indicating decomposition and interaction of peroxides with unreacted but active oxygen or fuel molecules. Surface had an inhibitory action on this second stage. During the reaction active "moloxides" [11] first form, are converted to more stable peroxides which may break down to water and an unsaturated compound which is in a condition to react further with oxygen. The secondary reactions give rise to formation of water, unsaturated compounds, fatty acids, carbon monoxide, carbon dioxide, aldehydes, etc. Soon after the peroxides have reached their maximum concentration, no more free oxygen is present in the mixture and further formation of "moloxides," peroxides, water, and fatty acids cannot occur. However, the further decomposition of peroxides present into carbon dioxide, carbon monoxide and other gases continues to give rise to a marked increase in pressure toward the end of the reaction.

Mondain-Monval and Quanquin [20] in studying the direct air oxidation of pentane, hexane, octane, and gasoline at about 300° C. found that aldehydes, carbon dioxide, and an oily yellow liquid with a strongly oxidizing reaction were formed. This liquid was found to belong to peroxides of the type R-O-OH where R represents methyl or ethyl radicals. The formation of these alkyl peroxides and their decomposition at higher temperatures was considered to explain the spontaneous ignition of detonating mixtures and the phenomena of flameless explosion and to support the peroxide theory of knocking and the action of antiknock compounds.

In studying the oxidation of hydrocarbons with a view to determining ignition temperatures and the effect of antiknock compounds, Dumanois [21] heated mixtures of air and gasoline from an initial condition of 20° C. and 5.3 Kg. pressure in a cylindrical bomb of 700 cc. capacity. Pressure was used as an indication of extent and kind of reaction. A point of inflection in the pressure curve was noted at 120° C. where the progressive pressure rise was less than that in the lower temperature range. At temperatures of from 200° to 250° C., depending on the composition of the mixture, a sudden rise in pressure occurred. The explanation advanced was that at 120° C. formation of peroxides began, these accumulated until the temperature had risen to about 210° C. when sudden decomposition occurred. However, with benzene-air mixtures there was no indication of peroxide formation, and no autoxidation below 300° C.

For large amounts of pentane up to about twenty times theoretical, the curve began to be sensibly linear after vaporization was complete, but was below that corresponding to mixtures of pentane and nitrogen, showed a point of inflection at 120° C. and then rose slowly to 10° to 15° C. below the ignition point. The temperature of spontaneous combustion fell as the amount of pentane used increased. The speed of combustion passed through a minimum at six times the theoretical amount of pentane, dimin-

[20] Mondain-Monval and Quanquin, *Compt. rend.* 191, 299 (1930).
[21] Dumanois, *Proc. 2nd Intl. Bit. Coal Conf.* (1928) Pittsburgh.

ished sharply at nine times and finally rose slowly. Carbon was deposited only when the proportion of pentane was from five to eight times theoretical.[22]

The induction period in a hexane-air mixture is greatly shortened by the addition of a small quantity of ethyl ether,[23] or by first passing it over a heated catalyst to form small concentrations of aldehydes and acids. But a small quantity of ethanol in paraffin hydrocarbon fuels facilitates combustion although it does not lead to an explosion. In such cases there is no induction period. The formation of peroxides is presumably prevented, there being no long induction period as found by Brunner and Rideal (loc. cit.), no rapid increase in oxidation, and no explosion.

Quantitative investigations of the reaction products showed Brunner[10a] that in addition to the assumed formation of moloxides and peroxides during the oxidation of hexane the formation of unsaturated intermediate products was of importance. These intermediates, formed by the splitting of hydrogen, took up oxygen to yield new, secondary peroxides which behaved in a manner comparable to the primary peroxides, to form aldehydes, peracids, water, and other products.

Berl, Heise and Winnacker[24] raise certain objections to the proposed peroxide mechanism and suggest the primary dehydrogenation of the paraffin hydrocarbon with the formation of an olefin which then adds an oxygen molecule to form a peroxide. In an attempt to discover the intermediate products formed in the oxidation of hexane, these workers used a gas mixture containing insufficient oxygen for the complete oxidation of hexane. This was passed into a combustion tube filled for 20 cm. of its length with a catalyst of iron oxide. Considerable water was formed and acidity, iodine number, and aldehyde content were determined for both the aqueous and non-aqueous fractions. The formation of water at 300° to 350° C., without the appearance of any oxides of carbon, indicated to them that the hydrogen split off before any carbon united with the oxygen. The high iodine number of the condensate confirmed their belief. At about 400° C. the product darkened and a tarry residue deposited on the cool parts of the tube, suggesting polymerization and condensation of unsaturated compounds and aldehydes. Ethylene and carbon oxides appeared at higher temperatures. Hydrogen and methane could not be detected. The bulk of the product was found to consist of aldehydes and acids particularly of three carbon atom chain length. Cyclohexane polymerized to yield a large amount of tar with no lower boiling products than the original hydrocarbon. At 600° C. benzene gave rise to a slight formation of carbon monoxide but no water. No more than traces of formaldehyde or water were found in any of the benzene experiments. Ethanol began to be oxidized to acetaldehyde at about 300° C. Between 400° and 500° C. aldehyde formation reached a maximum after which carbon

[22] Dumanois and Mondain-Monval, *Rev. Petrol* Nov. 10, 1928, p. 1568.
[23] Berl and Winnacker, *Z. Physik. Chem.* 148A, 36-44 (1930).
[24] Berl, Heise and Winnacker, *Z. physik. Chem.* 139A, 453 (1928).

monoxide became the chief product. At temperatures appreciably above 500° C. the combustion went to carbon dioxide. With anhydrous alcohol the reaction rate was 96 per cent less than for alcohol with water present.

The facts that paraffins do split off hydrogen on heating to form olefins which are presumably in a highly active state at the instant of formation and that when saturated hydrocarbons are decomposed in a current of nitrogen the iodine number of the condensate is lower than in the presence of oxygen have been cited by these authors in support of their theory. Washburn, Bruun, and Hicks have also found that the change in the iodine number of petroleum oils caused by heating up to 370° C. in air, or in hydrogen, nitrogen, or carbon dioxide is greatly reduced in the absence of air.[25]

In a study of the non-explosive oxidation of propane and butane Pease[26] classified the reactions as follows on the basis of gas analyses only.

(1) $C_3H_8 = C_3H_6 + H_2$
(2) $C_3H_8 + 1/2 O_2 = C_3H_6 + H_2O$
(3) $C_3H_8 + 2O_2 = CO + 2H_2O + CH_3CHO$.
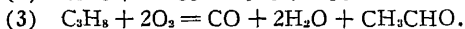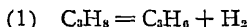
The first two reactions appeared at 500° to 600° C. and seemed to be more or less normal homogeneous gas reactions, subjected, however, to induction by reaction (3) at the lower temperatures. The third reaction begins at about 300° to 350° C. and indicates a chain reaction which is subject to suppression by packing in the reaction tube or by the use of a small tube. Such a proposed mechanism, although not supported by liquid analyses, indicates the formation of unsaturated molecules as have been found in the case of higher hydrocarbons and also indicates the possibility of forming olefins from saturated hydrocarbons by a process of oxidation rather than by "cracking."

The peroxide theory has been further criticized by Lewis,[27] who claims that Callendar's evidence for peroxide formation is inconclusive since it might have indicated hydrogen peroxide or peroxides formed from unsaturated compounds which were first formed. Hydrogen peroxide has been found[28] in the flames from illuminating gas, coke oven gas, and hydrogen. Lewis postulated the reaction of the split-off hydrogen with oxygen to form water and leave an unsaturated residue from which peroxides and aldehydes might later form. The pressure changes occurring during the oxidation of carefully purified amylene in bulbs, the temperature of which was slowly raised, were recorded as functions of the temperature. These curves show three sections: (a) a region deviating but slightly from the normal vapor pressure curve, (b) a gradual drop in

[25] Washburn, Bruun and Hicks, *Bur. Standards J. Research* **2**, 467-88 (1929).
[26] Pease, *J. Am. Chem. Soc.* **51**, 1839 (1929).
[27] Lewis, *J. Chem. Soc. (London)* **1927**, 1555-72; *ibid.* **1929**, 759-67; *ibid.* **1930**, 58-74.
[28] a. Engler, *Ber.* **33**, 1110 (1900); b. Schwartz, *Warme* **48**, 1, 17 (1925); c. Hauser, *Ber.* **56B**, 888 (1923).

pressure to a minimum point indicating slow reaction with a decrease in the number of molecules, (c) a sharp rise in pressure due to the decomposition of the products formed in (b), followed by nearly normal gas pressure. Analyses made during the first period gave positive evidence of reaction with formation of aldehydes, and carbon oxides, the amount of reaction increasing with the per cent of pentane in the mixture up to equi-molal amounts of hydrocarbon and oxygen. The point of occurrence of the minimum pressure of the second period varies from 240° C. with 17.8 per cent pentane mixture to 237° C. with a 62.2 per cent mixture and the drop in pressure is greatest in the equimolal mixture. Lewis suggests that peroxides formed during the first period decompose to aldehydes. Increase of temperature increases this decomposition and also promotes the polymerization of the aldehydes to account for the drop in the pressure during the second period. At the point of minimum pressure sufficient active molecules have accumulated to set up a chain reaction process to give rapid oxidation and rise in pressure.

The presence of 0.5 per cent of lead tetraethyl resulted in a linear relation between pressure and temperature and permitted only slow oxidation as evidenced by the presence of carbon oxides at the end. The decomposition of peroxides to form water increased the pressure above normal. The evidence is interpreted to support the idea that the combustion of a hydrocarbon is the oxidation of the unsaturated compound, first formed, to a peroxide which decomposed to give products in an active state which are further oxidized to water and carbon oxides.

In further support of his theory, Lewis notes that although cracked gasolines contain peroxide-forming substances, they show much less tendency to knock than do the uncracked gasolines. He suggests that antiknock compounds prevent the primary dehydrogenation of a saturated hydrocarbon to an olefin which is the necessary step according to his theory.

Chain Reactions

Chemical reactions which occur with finite rates show that all of the molecules present cannot be in the same energy state, otherwise they would occur with infinite speed if they occurred at all. Hence, encounters between molecules leading to reaction must be between those in an exceptional energy state. These molecules, called "active" must necessarily be present before reaction can occur. In general, the number of molecular collisions that occur to every collision that produces reaction is large, this proportion of ineffective to effective collisions depending on the relative number of "active" molecules present. The effect of temperature alone on the attainment of the high energy state was sufficient to lead Arrhenius [29] to explain the law of change of reaction velocity with temperature in terms of activation as follows:

[29] Arrhenius, *Z. physik. Chem.* **4**, 226 (1889).

$$\frac{d \log k}{dt} = \frac{A}{RT^2}$$

where A is the energy of activation.

Activation caused by collisions which produce reaction, corresponds to the simplest conception that reaction follows sufficiently violent collisions between two molecules, and does not differentiate between rate of reaction and rate of activation. However, in exothermic reactions such as those involved in the oxidation of hydrocarbons, the energy liberated may be passed on to molecules of the reactants and thus activate them more rapidly than normally. Such a process gives rise to a chain of reactions.

Evidence for the propagation of reaction chains in many different reacting mixtures has been obtained by different workers. Weigert and Kellerman [30] showed their presence in mixtures of hydrogen and chlorine, and Porter, Bardwell and Lind [31] studied the action of light and alpha particles on the reaction. Polanyi [32] showed that the chain reaction of hydrogen and chlorine could be initiated by reaction between sodium and chlorine. Vapors of alkali metals have also been found to produce reaction between chlorine and a hydrocarbon such as methane.

In the case of the reaction between hydrogen and oxygen, the first gaseous reaction to be studied [33] where stable and measurable chains occurred, the mechanism has been found to be influenced markedly by pressure. Thus, within certain limits explosive chains are set up from active centers of hydrogen peroxide:

$$H_2 + O_2 = H_2O_2$$
$$H_2O_2 + H_2 = 2H_2O *$$
$$H_2O * + O_2 = O_2 * + H_2O$$
$$O_2* + H_2 = H_2O_2$$
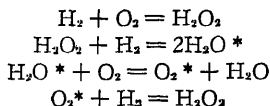
Again in other limits, evidence exists that the termolecular reaction

$$2H_2 + O_2 = 2H_2O$$
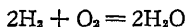
is the principal process starting reaction chains. Below 500° C. reaction takes place on the walls of the vessel, and the rate is not influenced markedly by pressure. The temperature coefficient is low. Between 540° and 590° C. another reaction comes into play. This is a gas reaction, of very high order and has a high temperature coefficient. This reaction is retarded by wall surface, quite different from the surface reaction occurring below 500° C. Hence, the probability that this reaction is chain-like in character is strong since the wall effect in suppressing the reaction suggests the deactivation or destruction of active molecules to break the chains. The presence of inert gases accelerates the reaction, the order being $H_2O >$ $A > N_2 >$ He. This points to a lengthening of the chains by the inert

[30] Weigert and Kellerman, *Z. physik. Chem.* 107, 1 (1923).
[31] Porter, Bardwell and Lind, *J. Am. Chem. Soc.* 48, 2603 (1926).
[32] Polanyi, *Trans. Faraday Soc.* 24, 606 (1928).
[33] a. Hinshelwood and Thompson, *Proc. Roy. Soc.* 118A, 170 (1928); b. Gibson and Hinshelwood, *ibid.* 119A, 591 (1928); c. Thompson and Hinshelwood, *ibid.* 122A, 610 (1929).
* Activated molecule.

gases, possibly by the action of elastic collisions between active and inert molecules to prevent deactivation at the walls.

Small amounts of nitrogen peroxide lower the ignition temperature of hydrogen in oxygen [84] by as much as 200° C., the limiting amount of nitrogen peroxide to produce the effect being sharply defined. As the amount of the peroxide is increased a second sharp limit is reached above which explosion does not occur and a very slow reaction takes place. The explanation offered for this action is that the notrogen peroxide can act both as a center for setting up reaction chains and as an inhibitor for destroying active hydrogen peroxide molecules. The relation of these two actions is dependent on the concentration.

Another phenomenon to be observed in the propagation of chains of reactions is the specific nature of the energy transfer. In the hydrogen and chlorine reaction active atoms are the transfer medium, in other reactions ordinary molecules at high energy levels are the active agents. The facts that inert gases do not destroy chains of reactions, and that activated chlorine molecules can survive many collisions before reacting with ozone molecules, together with other relative data have caused a recognition of this specificity.

The importance of chain reaction mechanisms in the oxidation of hydrocarbons lies in the effect produced by certain materials which when present in relatively small amounts act as negative catalysts in breaking the chains and suppressing reaction.[85] Because of relatively very small amounts of materials necessarily present to suppress markedly the fast reactions in hydrocarbon oxidation as compared to the catalyst required in positive catalytic reactions, workers have been led to explain the mechanism in ways other than by the removal of small amounts of positive catalysts. In other words, the action of inhibitors to certain oxidation reactions does not appear to be through the same effect produced by catalyst "poisons." If the reaction is taking place by a series of chains, then the destruction of a chain by the deactivation of an active molecule by the inhibitor not only prevents the reaction at the point but also prevents the reaction of all the other molecules which normally would have reacted in the chain. The effect of such inhibition is, of course, most marked in reactions occurring in very long chains for there the greatest number of molecules would be affected by a single molecule of inhibitor. Such long chains occur in the photo-chemical oxidation of benzaldehyde and heptaldehyde.[86] In the case of reactions, such as the oxidation of benzene, which occur through the probable mechanism of short reaction chains, inhibitors would have a much less apparent effect.[87]

Hydrocarbons may undergo an autoxidation in a manner similar to that in the case of aldehydes, drying oils, rubber, etc. In the case of these

[84] a. Gibson and Hinshelwood, *Trans. Faraday Soc.* 24, 559 (1928); b. Thompson and Hinshelwood, *Proc. Roy. Soc.* 124A, 219 (1929).
[85] Christiansen, *J. Phys. Chem.* 28, 145 (1924).
[86] Bäckström, *J. Am. Chem. Soc.* 49, 1460 (1927); *Trans. Faraday Soc.* 24, 601 (1928).
[87] Fort and Hinshelwood, *Proc. Roy. Soc.* 127A, 218-27 (1930).

latter substances the action of oxidation inhibitors has been successfully explained on the basis that the oxidation reactions were chain-like in character. The acceptance of a chain reaction mechanism for hydrocarbon oxidation does not involve any theory regarding the nature of the intermediates or of the steps involved other than that "active" molecules are formed which are capable of passing on their energy, and the chain mechanism is therefore not unique to a specified few substances. However, evidence exists that in hydrocarbon oxidation peroxides are formed which act as centers for the propagation of the chains of reactions and as this proposed mechanism fits considerable of the available data on antiknock action, it is looked on with favor by many prominent investigators in this field.[38]

For hydrocarbon combustion a mechanism has been proposed as follows. Molecules of oxygen and hydrocarbon both in a state of activation by virtue of a high energy content collide to form a temporary peroxide in a very high state of energy, which breaks into water and an aldehyde. Both of these product molecules have high energy contents since they must possess not only the initial energy of the oxygen and hydrocarbon but also the energy liberated by the reaction. They can collide with other molecules to result either in a reaction or a transfer of energy. Thus the reaction is continued and a chain produced.[17] The aldehydes formed in this way are also capable of forming peroxides and hence, of oxidizing autocatalytically.

Haber and Bonhoeffer [30] have studied the reaction in flames and explosions, and with the use of spectroscopic data, heats of dissociation, and other information have been able to postulate the type of reaction and the nature of intermediates formed during the combustion of such fuels as hydrogen, carbon monoxide, hydrocarbons. They observed the formation of such unstable substances as: OH, CH, CC, etc. They also showed that the chains could be destroyed by the loss of energy in the form of radiation which gave colors to the flame or explosion, different for the different fuels. Long-lived molecules in an exceptional state of energy may account for the luminosity of burning gas mixtures after oxidation is complete. Bone postulates that in combustion processes the molecular energy is largely vibrational and that a definite time interval must elapse before equilibrium is attained and the energy transformed to the kinetic state. From a study of the catalysis of the carbon monoxide flame by hydrogen, Garner [40] has concluded that the chemical energy is conserved within the flame by collisions between protons or electrons and the newly formed combustion products.[41]

The disclosures made by Pope, Dykstra and Edgar [42] in a study of

[38] *Compare* Moureu and Dufraisse, *Compt. rend.* 185, 1545-8 (1927); 186, 196-9 (1928).
[30] Haber and Bonhoeffer, *Z. physik. Chem.* 137, 263 (1928).
[40] Garner, *Ind. Eng. Chem.* 20, 1008 (1928).
[41] *Compare* Bone, *Nature* 125, 274-5 (1930).
[42] Pope, Dykstra and Edgar, *J. Am. Chem. Soc.* 51, 1875 (1929); 51, 2203 (1929); 51, 2213 (1929).

the vapor phase oxidation of the isomeric octanes have done much to clarify some of the ideas existing in regard to the combustion of hydrocarbons in the gasoline range of molecular weight. The facts that air was used as a source of oxygen and that the flow system permitted times of contact of quite short duration make the results of interest in interpreting the phenomena of internal combustion engine operation.

In the case of the oxidation of n-octane a practically constant amount of some substance reacting with potassium iodide was found in the product. This fact indicates the presence of peroxides formed from either the hydrocarbon, or aldehydes, or both, but does not demonstrate that this peroxidic compound is a primary product or of organic derivation. No alcohols at all were found. This fact is an added bit of evidence against the hydroxylation theory, since although the absence of alcohol has been explained on the basis of extreme ease of oxidation of this intermediate, it has been experimentally shown that alcohols even up to heptyl oxidize with difficulty in the absence of catalysts.[4a, 43] Up to 650° C. the formation of carbon dioxide is relatively unimportant. However, at 270° C. carbon monoxide appears suddenly in large amounts, accompanied by pressure surges and luminescent flashes. These phenomena, together with the fact that glass packing was found to suppress carbon monoxide formation without affecting carbon dioxide formation, strongly suggest a chain mechanism for the reaction producing carbon monoxide. The "activated" molecules require time for formation as evidenced by the accumulation of flashes toward the exit end of the reaction tube at the lower temperatures. As the temperature is raised the zone of flashing moves toward the inlet end and at high temperatures become smooth and continuous at this point. At temperatures of 660° to 670° C. and above the reaction becomes explosive with n-octane, while at 570° C. heptaldehyde and butyraldehyde mixtures explode, in all cases to water and carbon dioxide. However, the explosive combustion is not in itself complete as indicated by the appearance of luminescence between the explosion flashes possibly caused by further burning of the early products. In the lower temperature range of 200° to 250° C. the reaction probably represents formation of water and aldehydes. As the temperature is increased formation of carbon monoxide predominates and at 400° C. the reaction has produced aldehydes of the order of butyraldehyde or lower which at this temperature oxidizes more slowly. In the case of heptaldehyde a similar slowing down of the reaction is noticed when lower aldehydes have been formed. It is possible that the reaction products are similar at this stage. On the basis of these results the following mechanism has been advanced:

$$C_8H_{18} + O_2 = C_7H_{15}CHO + H_2O$$
$$C_7H_{15}CHO + O_2 = C_6H_{13}CHO + H_2O + CO$$
$$C_7H_{15}CHO + 1.5O_2 = C_6H_{13}CHO + H_3O + CO_2.$$
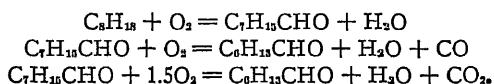
[43] Egerton and Gates, *J. Inst. Pet. Tech.* **13**, 244-73 (1927).

Thus it is the end of the hydrocarbon chain that is first attacked and the end of the aldehyde chain that is attacked in the successive reactions. Hydrogen and methane were not detected in the products.

Although Stephens [8] indicated that in the case of aromatics with aliphatic side chains the point of initial attack by oxygen was at a secondary carbon atom in the aliphatic chain, his experimental conditions differed from those of Pope, Dykstra, and Edgar. In the case of the isomeric actones, 3-methyl heptane, 3-ethyl hexane, 2-methyl-3-ethyl pentane, 2,5-dimethyl hexane, and 2,2,4-trimethyl pentane, the point of initial attack is again at a methyl group rather than at a secondary or tertiary carbon atom. However, there are certain striking differences in the way these isomers behave on oxidation under similar conditions. The hydrocarbons containing secondary or tertiary carbons are more resistant to oxidation than the straight chain molecules and the more condensed the hydrocarbon structure is the more resistant to oxidation it becomes. The curves representing amounts of oxidation products as functions of temperature are similar in shape for the different isomers. If a secondary carbon atom marked the initial point of attack of oxygen, rapid degradation of the molecule to low molecular weight compounds should result in a marked slowing down of oxidation.

The mechanism of the oxidation may be interpreted by the following steps. (1) Oxygen attacks the methyl group at the end of the longest open chain of the hydrocarbon to form water and an aldehyde, probably through the decomposition of initially formed peroxides. (2) The aldehyde is oxidized to a lower aldehyde, water, carbon monoxide, or carbon dioxide. (3) In the case of the branched isomers, this process continues until a branch in the molecule is reached, giving rise to a ketone instead of an aldehyde as the product. (4) Oxidation at low temperature slows down at this stage since ketones oxidize with more difficulty than aldehydes.

Although the oxidation of n-octene has been shown to begin at a higher temperature compared with n-octane, the process is otherwise similar and suggests that oxidation starts at the opposite end of the molecule from the double bond rather than at the point of unsaturation. It seems reasonable that all normal paraffin hydrocarbons of medium molecular weight follow the same course as n-octane. However, hydrocarbons such as 2,5-dimethyl hexane but of higher molecular weight might be attacked at the center of the molecule as well as the end. Condensed molecules like hexamethyl ethane are probably oxidized with difficulty since oxidation of the aldehyde could not occur as in the case of the n-octane.

Although the data of Layng and Youker [4a] were obtained in a bulb type of apparatus, they show the progressively increasing rate of oxidation of n-heptane, heptaldehyde, and heptoic acid and the stability of n-heptyl alcohol to oxidation (Fig. 32). No alcohol was found in the products from n-heptane oxidation.

The results of work on the knock rating of different pure substances

as fuels have shown the close parallelism existing between ease or mechanism of oxidation and the tendency to detonate in an engine. Thus, pure normal heptane (b.p. 98.4° C.) shows a pronounced tendency to knock, ignites at a low temperature,* and undergoes autoxidation. An octane, having a condensed molecule such as 2,4,4-trimethyl pentane

$$(CH_3—C—CH_2—CH—CH_3)$$

with CH_3 and CH_3 groups, (b.p. 99.3° C.) is a relatively non-knocking fuel and shows resistance to oxidation.[44]

Alcohols do not form peroxides when undergoing oxidation, oxidize at relatively high temperatures, and comprise non-knocking fuels.[45] Aromatic compounds as benzene and toluene have relatively high ignition temperatures and are excellent non-knocking fuels.

Definite relationships between molecular structure of hydrocarbons and tendency to knock have been found, which closely correlate the relationships existing between the structure and the tendency of paraffin hydrocarbons to oxidize.[42, 46] The relationship between molecular structure and tendency to knock may be characterized by the statement that in a homologous series the tendency to knock increases with increase in length of the carbon chain and in an isomeric series the tendency to knock decreases with increase in the number of side chains. The tendency to knock is also decreased by the successive introduction of methyl groups into a carbon chain of given length, and by practically a constant amount of methyl group added. The results of this work are best shown by Figure 33, in which the tendency

Fig. 32.—Oxidation of (A) pure n-heptane, (B) n-heptyl alcohol, (C) heptaldehyde, and (D) heptoic acid at 160° C. by oxygen in a closed bulb.[4a]

to detonate, expressed as aniline equivalent, is plotted against molecular weight. A positive aniline equivalent indicates that the compound knocks less than the reference gasoline. It represents the number of centigram-mols of aniline per liter that must be added to the reference fuel to produce a mixture that has a knocking tendency equivalent to that of a 1-molar solution of the hydrocarbon in the reference gasoline. A negative aniline equivalent indicates that the hydrocarbon knocks more than the reference fuel. It represents the number of centigram-mols per liter of aniline that must be added to the 1-molar solution of the hydrocarbon in the reference

* *Cf.* Ignition temperatures.
[44] Edgar, *Ind. Eng. Chem.* 19, 145 (1927).
[45] Ross and Ormandy, *J. Soc. Chem. Ind.* 45, 273-80T (1926).
[46] Lovell, Campbell, and lloyd, *Ind. Eng. Chem.* 23, 26 (1931).

gasoline to make it equivalent in tendency to knock to the reference gasoline.

It is of interest to note on this chart the increased range of knocking properties obtained with increased molecular weight of the hydrocarbon. The maximum knocking tendency of a given molecular weight paraffin
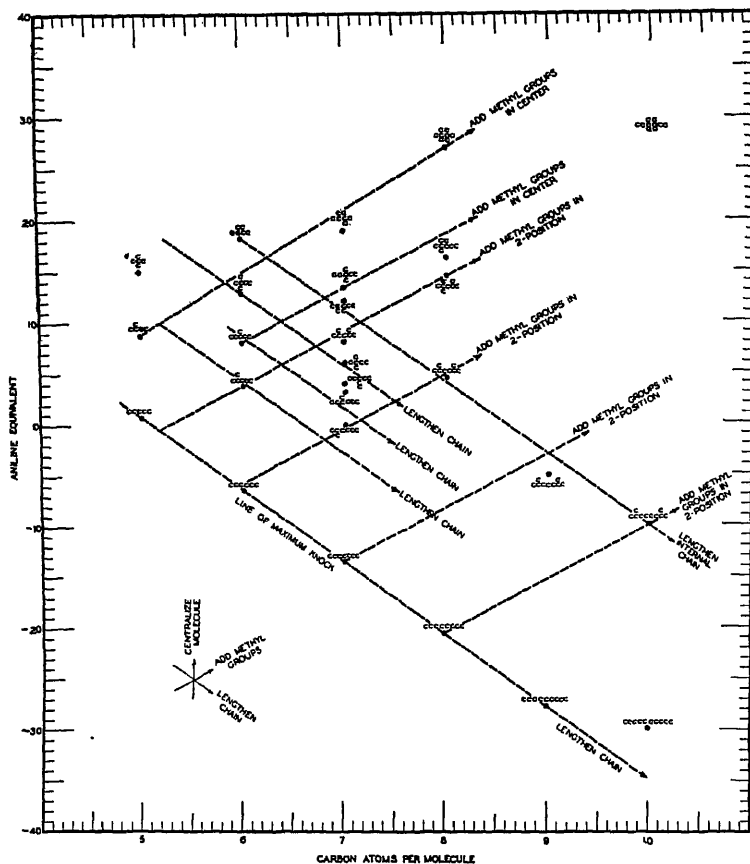
FIG. 33.—Relation between molecular structure and knocking characteristics of paraffin hydrocarbons. (Lovell, Campbell, and Boyd.)[40]

hydrocarbon seems to be represented by the straight chain isomer and the line on the chart connecting these points represents the line of maximum knock. Likewise the line through the points of minimum knock of the various isomers represents the limit of possibilities in this direction. The distance between these two lines constantly increases as the molecular weight of the hydrocarbons increase.

Inhibition of Oxidation

Considerable research work has been done in a study of the inhibition of the generally smooth oxidations occurring in liquid phase conditions.* Among the leaders in this work are Moureu and Dufraisse, who have applied the term antioxygenic activity to the effect produced by oxidation inhibitors. Notwithstanding that the greater part of this experimental work has dealt with liquid phase phenomena, the theories that have been evolved in explanation of some of the effects are directly applicable to vapor phase conditions, and hence to conditions existing in internal combustion engine operation.

Concisely, the important observation that the addition of relatively very small amounts of certain materials to readily oxidized substances inhibits the oxidation, has provoked the large amount of research devoted to the subject and has led to the formulation of theories which permit the prediction of results of proposed experiments as well as the explanation of puzzling results already achieved. The experiments have shown the very general character of inhibitor action and the necessity for a theory which involved but one constant, the presence of oxygen.

Figure 34 shows the effect of hydroquinone in suppressing the oxidation of benzaldehyde. Analogous results of the same order of intensity have been obtained by substitution for hydroquinone other phenols as well as other substances having a quite varied nature. Among these may be mentioned: pyrocatechol, pyrogallol, naphthols, tannins, iodine, inorganic halides, hydriodides of organic bases, ammonium iodides, alkyl iodides, iodoform, carbon

FIG. 34.—Effect of hydroquinone on the oxidation of benzaldehyde. (Moureu and Dufraisse.)[47]

1. Pure benzaldehyde.
2. Benzaldehyde plus 1/100,000 hydroquinone.
3. Benzaldehyde plus 1/20,000 hydroquinone.
4. Benzaldehyde plus 1/10,000 hydroquinone.
5. Benzaldehyde plus 1/2000 hydroquinone.
6. Benzaldehyde plus 1/1000 hydroquinone.

tetrachloride, sulfur, phosphorus, sesquisulfide, inorganic sulfides, amines, nitrites, amides, carbamides, urethanes, coloring matters, inorganic compounds of phosphorus, arsenic, antimony, bismuth, vanadium, boron, silicon, tin, lead, etc. The effects of these substances are, of course, varied but may be noticed with such a diversity of autoxidizable substances as: unsaturated hydrocarbons, complex organic compounds as fats, rubber, etc., sodium sulfite, aldehydes, etc.[47]

Some of these inhibitors may under certain circumstances act as positive catalysts for oxidation. Thus iodine and many iodine compounds act

* *Cf.* Milas, *Chem. Rev.* 10, 295-364 (1932).
[47] Moureu and Dufraisse, *Chem. Rev.* 3, 113-62 (1927); *J. Soc. Chem. Ind.* 47, 819-28, 848-54 (1928).

as positive catalysts in the autoxidation of styrene or linseed oil. However, pro-oxygenic activities are usually not very intense although some instances of intense action have been reported. In these instances of catalytic inversion the substances that have usually shown the most active anti-oxygenic activity with certain substances will be the most active pro-oxygenic catalysts with certain other substances.

The mechanism of autoxidation advanced by Moureu is similar in many respects to the peroxide theory. By the combination of an active molecule of oxygen with an active molecule of autoxidizable substance without the liberation of energy, a peroxide molecule of higher activity than the average of the mixture is formed. In this way an unstable system, the active peroxide molecule, is set up. This system may break down to form oxidized products, as occurs if no inhibition is allowed. These oxidized products, having a high energy level, are capable of further reaction with active oxygen or fuel molecules or of passing their energy to inactive molecules by inelastic collisions.[48] When the peroxide concentration reaches a critical value, chain reaction ensues, causing excitation and combination of molecules coming into contact with these active reaction centers.[18, 49] Or the system may revert to the normal stage of molecular oxygen and molecular autoxidizable substance by the liberation of energy to other molecules that may be present but without the formation of oxidation products. This view is essential to the hypothesis that anti-oxygenic activity is a manifestation of positive catalytic action as opposed to the view that it is due to the removal of positive catalysts for oxidation,[50] or to the view that the effect is due to inactivation of molecules ready to react and their return to a normal energy level.[51]

The mechanism that has been proposed for the action of the anti-oxidants is as follows. The combination of an active oxygen molecule with an active molecule of the oxidizable substance A results in the formation of an active peroxide $A(O_2)$. This peroxide, $A(O_2)$, may then oxidize the anti-oxidant, B, to form two peroxide molecules $A(O)$ and $B(O)$, which may destroy each other with the regeneration of the original components, A, B, and O_2. This reaction is extremely rapid and can take place with ease due to the proximity of the two molecules involved. It is possible that the anti-oxidant, B, may also react with an active oxygen molecule to form a peroxide, $B(O_2)$, which would be capable of destroying a molecule of $A(O_2)$ to regenerate A, B, and O_2. This reaction while of the rapid type involved in peroxide interaction is not favored by the nearness of the molecules, as is the preceding one. Depending on whether the peroxide, $B(O)$, reacts with $A(O)$ or with A the substance, B, will behave

[48] Moureu and Dufraisse, *Compt. rend.* 185, 1545-8 (1927); 186, 196-9 (1928).
[49] Graetz, *Ann. combustibiles liquides* 3, 69-76 (1928).
[50] a. Matignon, *Bull. soc. chim.* 31 (4), 228 (1927); b. Reiff, *J. Am. Chem. Soc.* 48, 2893 (1926); c. Brunner, *Helv. Chim. Acta* 10, 707 (1927); d. Warburg, *Ber.* 58, 1001 (1925).
[51] a. Taylor, *J. Phys. Chem.* 27, 322 (1923); b. Perrin, *Compt. rend.* 184, 1121-4 (1927); compare c. Moureu, Dufraisse and Badoche, *Bull. soc. chim.* (4), 35, 1564 (1924).

as an anti-oxidant or as an oxidation catalyst, a hypothesis supported by the fact that certain of the inhibitors behave as positive catalysts for the oxidation of certain substances. The pro-oxygenic reaction is favored by higher concentrations of the added substance, B. Because of the possibility for the occurrence of all of these reactions the net effect of the action of substance B will be the resultant of all of them.[50, 52] It is also possible for the substance, B, the inhibitor, to be converted from the peroxide form $B(O)$ into the stable oxidized form BO. Such a conversion results in a loss of active inhibitor and explains the loss of catalytic activity of the inhibitors over periods of time.[53]

Other theories that have been evolved also consider the action of inhibitors to be through the destruction of "active" intermediate oxidation products, such as peroxides, and the resultant interruption of a chain of reactions which normally would have involved many molecules of the oxidizable substance. Such theories differ principally in the mechanism through which peroxide destruction and chain interruption are brought about without the total concomitant destruction of the inhibitor.[54]

Based on the facts that the heavier paraffin hydrocarbons, which have the higher boiling points, are more prone to knock when burned in an engine and that the common antiknock dope, lead tetraethyl, boils at 200° C., Moureu was led to suppose that the action of antiknocks occurred in the liquid phase and that knocking originates in this phase with the high-boiling paraffin hydrocarbons.[55, 4b] The general anti-oxygenic theory has, hence, been considered applicable to the case of antiknock action. Here the antiknock dope has been assumed to hinder the formation of peroxides by an action similar to that manifested in the case of the usual liquid phase oxidation inhibition.[16]

The close parallelism found to exist between ease of autoxidation and susceptibility to knocking for several fuels supports the peroxide theory of knock induction and suppression. Ricardo [56] and Ostwald [57] classified the fuels according to increasing tendency to knock as follows: ethanol, xylene, toluene, benzene, tetra-hydronaphthalene, oxygenated naphthenes, cyclohexane, hexahydrotoluene, methanol, hexane, decahydro-naphthalene, lamp petroleum, heptane, high-boiling petroleum oils, ethyl ether. On the other hand, the tendency for these fuels to autoxidize is in the same order, i.e., alcohol, and benzene—very slight, paraffin hydrocarbons—increasing tendency as molecular weight increases, ethyl ether—very easily.[47] In general, fuels which cause knocking, autoxidize through formation of peroxides and are somewhat inhibited toward this oxidation

[52] Moureu and Dufraisse, *Compt. rend.* 184, 1121 (1927).
[53] Moureu and Dufraisse, *Rec. trav. chim.* 43, 645 (1924).
[54] a. Bäckström, *J. Am. Chem. Soc.* 49, 1460-72 (1927); *Medd. Vetenskapsakad. Nobelinst.* 6, No. 15, 34 pp. (1927); *Trans. Faraday Soc.* 24, 601-5 (1928). b. DuPont and Allard, *Compt. rend.* 190, 1419-21 (1930).
[55] *Compare* a. Egerton and Gates, *Nature* 119, 427 (1927); b. Dumanois, *Compt. rend.* 186, 292 (1928).
[56] Ricardo, *Auto. Eng.* 11, 92 (1921).
[57] Ostwald, *Brennstoff Chem.* 2, 17 (1921).

in the liquid phase by the presence of such antiknock dopes as lead tetra-ethyl, lead tetrapropyl, iodine, sulfur, phenyl sulfide, aniline, diphenyl-amine, triphenylamine, etc.[58] The effects of these substances as liquid phase oxidation inhibitors and as antiknock agents are not directly parallel.[59] Hence, although it cannot be denied that the phenomena taking place during the so-called induction period of the oxidation of a fuel[60] are of great importance, it is not equally clear that this explanation is the correct one. It seems more probable that vapor phase conditions must be recognized as the seat of the phenomena giving rise to knocking and the suppression of knocking.

Thus, α,α- and β,β-dinaphthylamines, and hydroquinone markedly check autoxidation of paraffins at 160° C. but lead tetraethyl and other anti-knocks have but little effect.[59] Layng and Youker found that in compari-son with lead tetraethyl in the gas phase, diphenylamine had a hundred times the effectiveness as an oxidation inhibitor as it possessed as an antiknock dope. Some distinction evidently must be made between inhibitors which act at low or moderate temperatures and antiknock dopes which alter combustion phenomena but do not affect low temperature oxidation. Moureu, Dufraisse and Chaux explain the ineffectiveness of lead tetraethyl at low temperatures as due to extreme ease of oxidation but this has not been demonstrated. On the contrary it has been shown that the effective antiknock dopes are not readily oxidized by air.[61]

In studying the slow oxidation of hexane-air mixtures (42 per cent hydrocarbon) at 200° to 210° C. Brunner found that there was an initial induction period, during which no reaction was detected.[19b] This was followed by the true reaction resulting in the formation of peroxides, water, aldehydes, acids and carbon oxides. Oxygen first added to the molecule to form unstable peroxides which decomposed to give water and an unsaturated compound. Aniline which was used as an inhibitor was oxidized at the end of this induction period and was, hence, active only during the initial stages of the oxidation. This effect of rapid destruction of the inhibitor by oxidation is in keeping with the contentions of Moureu.

The smooth, liquid phase oxidations that are inhibited by anti-oxidants occur at constant conditions of temperature and pressure and with a constant transmission of energy by chain reactions. The action of the inhibitor is to break these chains by a dissipation of the energy and thus to inhibit reaction. Quite the contrary is true in combustion occurring in an engine cylinder. Here reaction takes place at a constantly accelerated rate and at a constantly increasing temperature and with an increasing transmission of energy. Here the energy value of the chain increases until it reaches a point where the antiknock dope is affected, so as to oxidize

[58] a. Moureu and Dufraisse, *Chimie et. Industrie* 17, 531-5 (1927); 18, 3-12 (1927); b. Hatta, *J. Soc. Chem. Ind. (Japan)* 28, 1346 (1925); c. Mead and Cabe, *Brennstoff Chem.* 7, 303 (1926).
[59] Moureu, Dufraisse and Chaux, *Ann. combustibiles liquides* 2, 233-52 (1927).
[60] a. Ormandy and Craven, *J. Inst. Pet. Tech.* 10, 335 (1924); b. Dixon, *Rec. trav. chim.* 44, 305 (1925).
[61] Charch, Mack, and Boord, *Ind. Eng. Chem.* 18, 334 (1926).

or decompose and break the chain of energy passing along the reaction. If the chain is not broken, the shock wave and surge of energy which characterize knocking are developed. Thus, in internal engine combustion the chain may not be broken at the start but only after an energy level sufficient to affect the antiknock dope has been reached. The fact that knock inhibitors have a small but positive effect in retarding low temperature oxidations or in raising the temperature level necessary for oxidation to occur may be attributed to the possibility that even in low temperature, liquid phase oxidations some of the molecules may attain sufficiently high energy levels to be affected by the inhibitor.[24, 43, 62]

IGNITION TEMPERATURES

Although there appears to be no perfectly general relation between the experimentally determined ignition temperatures of fuel-air mixtures and the knocking tendencies of the fuels when used in internal combustion engines, many substances having high auto-ignition temperatures do not cause knocking in engines and some having low auto-ignition temperatures do cause knocking. Also the consensus of opinion is that in general knock inducers lower and knock suppressors raise the ignition temperature of a fuel.[63] Because of this apparent importance of the temperature at which different fuels ignite in relation to their tendency to induce or suppress knocking in engines and of the possible indications that might be had of the way in which antiknock dopes function, a considerable amount of work has been done in measuring ignition temperatures with and without antiknock compounds being present and under a great variety of conditions.

The parallelism existing between the ignition temperature of a fuel and the highest useful compression ratio, H.U.C.R., when the fuel is used in an internal combustion engine is shown by Table XXII.

TABLE XXII.—*Relation Between Ignition Temperature and H.U.C.R.*[63, 64]

Fuel	Ignition Temp. ° C.	H.U.C.R.
Petrol	(460)	5.1–5.5
Pentane	515	5.7
Hexane	470	4.8–5.1
Heptane	430	3.7–4.7
Cyclohexane	535	6.0
Benzene	675–710	6.9
Toluene	>760	>7.0
Xylene	>760	>7.0
Ether	440	3.5–4.0
Alcohol	515	7.0

Straight run gasolines show a regular relation between auto-ignition temperatures and knock rating. Cracked gasolines, on the other hand, do

[62] Weerman, *J. Inst. Pet. Tech.* **13**, 300 (1927).
[63] a. Boord and Schaad, *Bull. Pet. Div. Am. Chem. Soc.* Sept. 1924; *compare,* however, b. Aubert, Pignot and Villey, *Compt. rend.* **185**, 1111 (1927), who contradict this.
[64] *See also* Egerton and Gates, *Proc. Roy. Soc.* **114A**, 137-51 (1927).

not show such a regular relation. Nash and Howes compared the ease of oxidation of olefins by potassium permanganate with their antiknock action.[65] They found that while olefins of lower molecular weight could be easily oxidized, the higher ones, especially those with branched chains, were only acted on with difficulty. In general those most easily oxidized were the least effective against knocking. Di-isobutylene is but slowly oxidized and is of good non-knocking quality. The olefins, in general, had better knock ratings than the aromatics.

In general the ignition point of an air-fuel mixture is the temperature at which the rate of gain of heat from the reaction balances the rate of heat loss as the rate of oxidation is increased. If this temperature is exceeded, the reaction accelerates until sufficient energy is being liberated in the visible part of the spectrum for the point of inflammation to be reached.

The determination of the ignition temperature is largely empirical, and the actual values experimentally obtained depend on many variables. However, the ignition temperature of a substance under a given set of conditions is quite definite. Difficulties have arisen largely because investigators have tried to make comparisons between ignition temperatures determined under different experimental conditions and because it has not definitely been known which of the several methods would more nearly simulate conditions existing during the combustion in internal combustion engines.

The methods most largely used have been: (1) explosion of gaseous mixtures by adiabatic compression, (2) explosion of gaseous mixtures under different initial pressures by gradual heating, (3) mixing preheated streams of gas and air, (4) dropping a liquid fuel into a hot cup through which heated air was passing.

In methods (1) and (3) the time possible for the preliminary interaction after mixing had occurred is negligible. In methods (2) and (4), however, preliminary reaction may occur and the effect of an unkown factor corresponding to the induction period is introduced. Nevertheless, a large amount of data has been obtained by method (4) in which the liquid fuel is permitted to fall into a heated cup in the construction of which many different materials have been used. The possible variations in procedure of this latter method has given rise to much discrepancy in published results. For comparative purposes among themselves the data of a single investigator are often quite useful particularly if a sufficient range of substances has been studied.

The method used by Moore [66] of dropping liquid fuel into a heated cup into which a stream of air is passing has been widely used. These values are relatively high because of the small volume of the cup which was used. In the same way the data of Hahn fail to show the possible

[65] Nash and Howes, *J. Soc. Chem. Ind.* 49, 113T (1930).
[66] Moore, *J. Inst. Pet. Tech.* 6, 186 (1920).

minimum ignition temperature because of the small area of his ignition surface. The results of Constam and Schlapfer, obtained by use of a platinum cup, are possibly in error because of the catalytic action of this substance.[67] Some of the data taken by the method used by Moore have been obtained with oxygen and hence, are not directly comparable with data in which air was used.[68] Thompson obtained the most consistent results by using a 125 cc. round bottom Pyrex flask in a solder bath and by determining the ignition temperature always by the appearance of flame. This method is open to the objection that considerable time lag was permitted in determining the minimum ignition temperatures. In general the more rapid the ignition is, the higher the temperature shown for ignition. The work of Masson and Hamilton carried out with a small area heating surface and incompletely confined vapor showed high values.

The effect of time lag before ignition has been studied by Moore, Neumann, and Tizard and Pye each of whom used a different method for ignition.[69] By the cup method, Moore found that by successively decreasing the time lag prior to ignition from 25 seconds to 1.4 seconds the ignition temperature of gasoline in oxygen rose progressively from 284.5° to 320° C. In igniting heptane-air mixtures by adiabatic compression, Tizard and Pye showed that by reducing the time lag from 0.58 second to 0.05 second the ignition temperature rose from 282° C. to 324° C. This effect is also shown by the work of Berl, Heise, and Winnacker,[70] who used air compressed to 20 atmospheres and heated the air-fuel mixtures slowly in a closed chamber. Precombustion occurred and the flash point was determined by the sudden change of pressure shown by a manometer. For n-pentane and hexane, cyclohexane, cyclohexene, benzene, toluene, xylene, aniline, and alcohol the flash point temperature was lower than those shown by Tausz and Schulte, Tizard or Masson and Hamilton. The data show that had the mixtures been more rapidly heated, considerably higher flash points would have been obtained.

During the slower heating, autoxidation with formation of peroxides may occur and result in a final lower temperature being required for rapid combustion.[18] Thermal decomposition, rearrangements, etc., of the fuel molecules may also occur during this interval and result in lower temperatures being required for ignition.

When paraffin-air mixtures are heated in a closed bulb there is first a slow, progressive pressure rise up to a critical temperature,[71] called by Lewis[27] the critical inflexion temperature, C.I.T., at which rapid chemical action takes place with an increase in the number of molecules and a rise in pressure. This rise of pressure is more abrupt the slower the rate of

[67] Constam and Schlapfer, *Z. Ver. deut. Ing.* **57**, 1489 (1913).
[68] a. Tausz and Schulte, *loc. cit.;* also *Z. Ver. deut. Ing.* **68**, 574 (1924); b. Sinnot and Moore, *J. Soc. Chem. Ind.* **39**, 72 (1918); c. Ormandy and Craven, *J. Inst. Pet. Tech.* **10**, 335 (1924); **12**, 650 (1926); d. Tanaka and Nagai, *J. Soc. Chem. Ind. (Japan)* **28**, 487 (1925); **29**, 266-72 (1926).
[69] a. Neumann, *Z. Ver. deut. Ing.* **68**, 574 (1924); *see also* b. White and Price, *J. Chem. Soc. (London)* **115**, 1462 (1919); c. Bridgeman and Marvin, *Ind. Eng. Chem.* **20**, 1219 (1928).
[70] Berl, Heise, and Winnacker, *Chaleur & ind.* **10**, 179-87, 241-6 (1929).
[71] Mondain-Monval and Quanquin, *Ann. combustibiles liquides* **5**, 307-24 (1930).

heating, indicating an accumulation of intermediates which react rapidly at a certain temperature level. Also as the rate of heating is increased, the ignition temperatures of paraffin hydrocarbons are increased, although those of the olefins are not greatly influenced. The temperature for this sudden rise in pressure is dependent upon the molecular weight of the hydrocarbon. Thus, for pentane it is 253° C., for hexane 232° C., and for octane 198° C. The C.I.T. for isopentane is slightly higher than that for the normal compound, 260° C. as compared with 253° C. In small bulbs a somewhat higher value was obtained than in large bulbs. Thus for heptane in a large bulb the C.I.T. is 210° to 212° C. and in a small bulb 214° to 215° C. In general, the C.I.T. is lowered by increased molecular weight, is lower for normal hydrocarbons than for isomers, is paralleled by the spontaneous ignition temperature, and is raised by the presence of surfaces or of lead tetra-ethyl. The facts point to the presence of peroxides in the early period of the reaction and the propagation of reaction chains from the active centers then formed, which are destroyed by surfaces or by dopes like lead tetraethyl to slow down the reaction. Since the point of ignition represents the condition at which the rate of generation of heat by reaction equals the rate of dissipation of heat from the reaction mixtures, a slower reacting mixture should require a higher temperature for this condition to exist. On the other hand, Dumanois [72] considers that antiknock agents simply retard ignition without actually changing the minimum temperature of spontaneous ignition.

Oxygen concentration has also been found to have a pronounced effect on ignition temperature. Mason and Wheeler,[73] using an electrically heated quartz tube as an ignition chamber and the dynamic flow method found that the ignition temperature of pentane in oxygen was lowered from 548° C. to 476° C. by increasing the pentane concentration from 1.50 per cent to 7.65 per cent.

The experiments of Mondain-Monval [74] and of Dumanois [21, 75] show the effect of fuel concentration on the ignition point in bomb systems. The auto-ignition temperatures for pentane and benzene were determined by introducing the supply of liquid into a 700 cc. cylindrical bomb, impressing 5.3 Kg. air pressure above atmospheric at 20° C. and slowly heating. A pressure record was taken. The results show that if the volume of pentane is less than the theoretical amount for complete combustion, 0.5 cc. liquid, ignition does not occur below 300° C.[27] However, at 250° C. a sudden rise in pressure occurs after which the pressure-temperature curve regains the slope it had before the rise. If the volume of liquid fuel is 0.5 cc. (theoretical), the pressure-temperature curve shows a dip at 120° C., and a sudden rise at 220° C., and auto-ignition, evidenced by a violent explosion, takes place at 230° C. No carbon is deposited

[72] Dumanois, *Compt. rend.* 182, 1526-8 (1926).
[73] Mason and Wheeler, *J. Chem. Soc. (London)* 125, 1869 (1924).
[74] Dumanois and Mondain-Monval, *Compt. rend.* 187, 892-4 (1929); *Ann. combustibiles liquides* 3, 761-78 (1928).
[75] Prettre, Dumanois and Laffitte, *Compt. rend.* 191, 329-31 (1930).

and the condensate is slightly acid. When the liquid volume taken is 0.5 to 2.0 cc., the explosions are less violent and occur at a lower temperature, being 228° C. for 1 cc. of pentane. No carbon is deposited. With 2.5 to 4.0 cc. of pentane auto-ignition takes place at 226° to 220° C., being preceded by a pressure increase. Carbon is deposited by the reaction which is more like a combustion than an explosion. With volumes of 4, 5, and 10 cc. ignition occurs at 220° C. and no carbon is deposited.

The minimum concentration of hydrocarbon necessary to obtain explosions by the method of heating with oxygen in closed bulbs increases rapidly with the molecular weight. Thus, with hexane no explosions occur below 10 per cent hydrocarbon concentration, and with octane the minimum concentration necessary is 33 per cent when a heating rate of 1° C. per minute is used. Diiso-amyl failed to ignite at this rate of heating at any concentration. Lewis observed no distinction between explosion temperature and "critical inflexion temperature."

Maxwell and Wheeler[76] studied the inflammation of mixtures of ethylene, propylene and butylene with air in a closed spherical bronze vessel. While the results were obtained with hydrocarbons largely out of the range of molecular weight of those used as fuel for automotive internal combustion engines, they are of interest for certain reasons. For mixtures of a given combustible with air, the flame temperature is the factor determining the mean rate of pressure development. The displacement of the observed maximum pressure mixture from the theoretical mixture for complete combustion toward excess hydrocarbon may be attributed to the effect of dissociation, since the calculated values for which allowance for dissociation is made show similar displacement.

The material of which the ignition cup is made has an effect on the temperature at which the fuels ignite. Thus Callendar found the following temperatures for n-hexane: cast iron—255° C., lead—225° C., aluminum—284° C., tin, nickel and zinc not noticeably different from glass, copper and carbon slightly lower than in glass, platinum black 170° C., and glass—265° C. Thompson found copper, low carbon steel, and chromium surfaces to give slightly higher results for n-hexane than glass. Masson and Hamilton found the auto-ignition temperature of nitrobenzene to be 556° C. on platinum and 513° C. on silver, and of aniline to be 620° C. on both surfaces.[77] Catalysts that do not promote oxidation or have a slow action, such as polished zinc and tin have very little effect on ignition temperatures or time lag prior to ignition.[78]

From the results of their work on the effect of pressure on ignition temperature, Tausz and Schulte concluded that the effect was so variable that no predictions could be made from atmospheric data as to what the temperatures would be under pressure.[99c] This uncertainty is due largely to the influence of other complicating factors, such as the effect of pressure

[76] Maxwell and Wheeler, *J. Chem. Soc.*, 1927, 2069-80; 1929, 245-51.
[77] *Compare* Edgar, *J. Soc. Auto. Eng.* 22, 41 (1928).
[78] Lewis, *J. Chem. Soc. (London)* 1930, 2241-54.

TABLE XXIII.—*Ignition Temperatures in Degrees Centigrade of Various Organic Liquids.*

Substance	M	H	T.S.	E.G.	T.N.	S(R)	T.P.	T	WP	MH	C	B
Benzene	566	520	740	700				580		656	670	588
Xylene	484	500	(662)	780				539		618	540	514
Toluene	516		810	780				553		633		624
Cyclohexane			(552)	536	(513)	419(R)	370					
Methyl cyclohexane				470	(318)	387(R)	324	309				400
Pentane (1)				515	(312)		316			579		
Pentane (2)				540	(285)							446
Hexane			487	525	(322)	366(R)	307	248		520		
Isohexane			(268)	430	(298)						266	338
Heptane					(290)	330(R)	298	233				
Decane			463 (202)									
Ethyl ether	347	400	343 (178)	440	(200)		227	193	187	487	145	
Ethanol	518	510	558 (425)	515	(340)	510		426	465	568	445	404
Acetone	(395)		700 (568)		(504)	570		636				
Acetaldehyde			185 (140)	395 impure								
Benzaldehyde			180 (168)			380						
Carbon bisulfide				120						343		
Aniline	770		770 (530)	750		530	226	125		620		568
Xylidine			715 (574)	820								
Dimethylaniline				440								
Benzonitrile				625								
Phenol			295 (270)	730, 500, 320								
Kerosene	(380)				(267)							

TABLE XXIII.—Cont.

Petrol	383 (272)		(310)		
Iso-amyl alcohol	(555)	553			450
Methanol	505	470	(513)		440
n-Propanol	(445)	433	(328)		
Isopropanol	590	456	(512)		570
n-Butanol	450 (385)	367	(334)		
Isobutanol		441	(364)		
Tert.-butanol		483			
Benzyl alcohol		436			390
Gasoline (Socony)		258			
Amyl alcohol	409 (390)				
n-Octane		275		519	

( ) Results with oxygen.
M Moore, *J. Soc. Chem. Ind.* **36**. 109 (1917).
H Holm, *Z. angew. chem.* **26**. 273 (1913).
TS Tausz and Schulte, *Mitt. chem.-tech. Inst. tech. Hochschule Karlsruhe* **2**. 1 (1924).
E.G. Egerton and Gates, *J. Soc. Pet. Tech.* **13**. 256 (1927).
TN Tanaka and Nagai, *Proc. Imp. Acad. Tokio* **2**, 221 (1926); *J. Soc. Chem. Ind. (Japan)* **29**, 266-72 (1926); cf. ibid. **28**, 487 (1925).
TP Tizard and Pye, *Phil. Mag.* **44** (6), 79 (1922).
T Thompson, *Ind. Eng. Chem.* **21**. 134 (1929).
WP White and Price, *J. Chem. Soc.* **115**. 1248 (1919).
MH Masson and Hamilton, *Ind. Eng. Chem.* **19**. 1335 (1927); **20**. 813 (1928); **21**, 544 (1929).
A Aillaire, *Compt. rend.* **168**. 729 (1919).
C Callendar, *Engineering* **123**. 147, 182, 210 (1927).
R Ricardo. *Rept. Empire Motor Fuels Com.—Inst. Autom. Eng.* **18**. part 1 (1924), p. 148; cf. Callendar, King and Sims, *Engineering* **121**. 475 (1926).
B Berl, Heise, and Winnacker, *Chaleur & ind.* **10**. 181 (1929).

in changing the necessary composition of fuel-air mixtures capable of inflammation, etc.[70]

In the case of mixtures of fuels the ignition temperature is usually nearest to that of the component with the lowest ignition point, provided it is present in greatest amounts. Thus, a small amount of acetaldehyde added to pentane makes little difference in the ignition temperature, although the aldehyde alone ignites at a much lower temperature.[17] In this case the reaction chains inducing the oxidation of acetaldehyde alone cannot be effective in the mixture because of the ineffectiveness of collisions with hydrocarbon molecules of low energy content. A small amount of ethanol added to saturated paraffin hydrocarbon fuels facilitates combustion but does not promote explosions in the air-vapor mixtures. The addition of small amounts of ethyl ether to hexane-air mixtures, which ordinarily have a long induction period, greatly shortens the lag and leads to the explosion of the mixture.[23]

Table XXIII although by no means complete gives the values obtained by a variety of methods for ignition temperatures of a number of the more common combustible liquids, and furnishes a basis of comparison.

The ignition of fuel-air mixtures by adiabatic compression makes use of the relation:

$$\frac{T}{T_0} = \left(\frac{P}{P_0}\right)^{1-\frac{1}{\gamma}} = \left(\frac{V_0}{V}\right)^{\gamma-1}$$

for rapidly heating the combustible mixture to ignition temperature. The time lag during the compression stroke while the temperature is being brought up to the ignition point can be made very short and is largely determined by the mechanical difficulties involved in suddenly stopping a rapidly moving piston without vibration and in recording the pressure and temperatures developed as functions of time.[79]

A number of workers have used this method for determining ignition temperatures and approached true adiabatic compression to various extents. The data of Tizard and Pye, and of Ricardo are shown in Table XXIII. The apparatus difficulties, however, have retarded the more general use of the method.[80]

Cause of the Knock

As much controversy has existed regarding the cause of the actual knock in an engine as exists in regard to the mechanism of the combustion and action of antiknock dopes during engine operation, and a number of theories has been proposed, the very diversity of which indicates their inadequacy. Just as in the case of oxidation mechanism studies, a large number of experiments have been performed at other than conditions

[79] *See* Smith, D.Sc. Thesis (1930) Mass. Inst. of Tech., Cambridge, for details regarding apparatus.
[80] *See also* a. Aubert, Pignot, and Villey, *Compt. rend.* **185**, 1111 (1927); b. Pignot, *ibid.* **182**, 376-7 (1926); *J. usines gaz* **50**, 293-8 (1926); c. Dixon, Bradshaw, and Campbell, *J. Chem. Soc.* (*London*) **105**, 2027 (1914); d. Duchene, *Compt. rend.* **186**, 220 (1928).

existing in the engine cylinder for the purpose of examining the phenomena related to explosion and detonation. The following factors [81] involved in such work have not all been considered by the workers with the result that much of the data available are not directly comparable: 1. Closed and open end tubes; 2. Diameter of tubes; 3. Texture of tubes; 4. Composition of tubes; 5. Change in tube diameter; 6. Length of tube; 7. Chemical composition of fuel; 8. Composition of gas mixture; 9. Composition of secondary gas; 10. Turbulence; 11. Gaseous ionization and excitation; 12. Method of ignition; 13. Temperature of ignition; 14. Compression; 15. Dilution; 16. Pressure. Also, in experiments that have been performed in actual, operating engines the conditions have been far from uniform. Variations in such factors as: 1. Size and shape of engine piston and size of cylinder; 2. Shape of cylinder head; 3. Type of valves; 4. Method of cooling; 5. Carburetor setting; 6. Mixture ratio; 7. Humidity of air; 8. Spark location and kind of spark plug; 9. Spark intensity; 10. Engine speed; 11. Compression ratio; 12. Turbulence, have made it practically impossible to correlate data of independent investigators.[82] Furthermore, considerable of the data have not been of a nature to make them readily adaptable to an explanation of the phenomena under consideration. Recent work in the General Motors Research Laboratories with different fuels in special engines has done much to clarify the ideas regarding the mechanism of knocking and its suppression.

Mechanical knock theory. Dickinson [83] advanced the theory that the knock was due to an impact of metal parts in the engine cylinder but does not explain the origin of the pressure or force which supposedly caused the impact.

Dissociation theory. The dissociation theory of knocking, based on the hypothesis that a sharp increase of pressure produced by high temperature dissociation of hot gases caused a knock, is unsound because dissociation has been shown to occur to only about 5 per cent and to develop a pressure rise too slowly to produce a knock.[81]

Nuclear drop theory. From a consideration of the temperature-entropy diagrams of the saturated vapors of fuels, Callendar [84] was led to propose that nuclear drops of the higher boiling constituents of the fuel or of high boiling fuels might be present in an engine cylinder at the moment of ignition of the fuel-air mixture. These nuclei would form easily ignited points since the higher members of a hydrocarbon series are more easily ignited, and would thus become foci for the ignition of the unburned charge. He attributed the cause for the knock to the sudden ignition of a large volume of the charge and the resultant sudden increase of pressure, and further suggested that absorption of radiant energy would increase the effect and that carbon particles would likewise induce ignition.

[81] Clark and Thee, *Ind. Eng. Chem.* 17, 1219 (1925).
[82] Wilson, *Am. Soc. Test. Materials, Symp. Devel. Autom. Materials,* Detroit, March, 1930.
[83] Dickinson, *J. Soc. Autom. Eng.* 8, 558 (1921).
[84] Callendar, King and Sims, *Engineering* 121, 475,509,542,575 (1926).

Analogy is drawn to the objectionable "preignition" caused by the ignition of the fuel mixture directly in contact with hot spots on the cylinder or piston head, by showing that the nuclei act as hot spots throughout the mixture to inflame a considerable portion at one time.

An objection to this theory is that it has been based on data from the saturated vapors of the fuels and not from dilute air-vapor mixtures. The existence of liquid drops in the dilute fuel mixture drawn through the carburetor, hot intake manifold, and mixed with the hot residual gases in the hot cylinder is doubtful. Also, the fact that such extremely volatile fuels as ethyl ether knock strongly cannot be explained. The fact that some of the most volatile gasolines knock more readily than heavier grades has been attributed to the presence of impurities in the latter which act in an antiknock capacity.

Molecular collision theory. The molecular collision theory proposes that undecomposed hydrocarbon fuel molecules directly in front of the explosion wave will be bombarded and thus activated by the highly active molecules from the explosion wave itself. Garner and Saunders [85] studied this phenomena by means of the spectra of acetylene air detonations. They explain the formation of carbon in such detonations by the decomposition of acetylene into $2C$ and H_2 by the action of molecular collisions. The application of this theory to the mechanism of the action of antiknocks in internal combustion engine operation is not clear.

Free hydrogen theory. The excessively rapid combination of hydrogen with oxygen has been proposed as the cause of knocking. The hydrogen was supposedly liberated by the cracking of hydrocarbons present in the gasoline prior to any extensive oxidation. Acetylene likewise has a high rate of reaction with oxygen and may also be formed by hydrocarbon cracking. The facts that the rates of flame propagation of these two substances is from six to ten times that of gasoline-air mixtures and that the presence of hydrogen or acetylene in gasoline-air mixtures increases the rate of flame propagation supports the theory. Also, the presence of such substances as iodine which vaporize with the gasoline and also combine with hydrogen is known to stop the knock and supports the theory. However, the necessity for explaining the mechanism of this cracking and in correlating the cracking rate with flame propagation rate and detonation phenomena detracts from the hypothesis.

Flame vibration theory. When combustible mixtures are ignited in tubes, the flame may begin to vibrate violently after traveling a certain distance. Detonation may or may not be set up in such cases, but the rapid vibrations generate a high pitched note that resembles certain types of knock. Morgan [86] has associated this note with the knock obtained in engine operation. From a study of the rate of flame propagation and the nature of vibrations obtained from methane and coal gas-air mixtures in

[85] Garner and Saunders, *J. Chem. Soc. (London)* 127, 77 (1925).
[86] Morgan, *J. Soc. Autom. Eng.* Jan. 8, 1925.

tubes one and two feet long, he concluded that vibrations were most likely to occur in very inflammable mixtures. Although this explanation may apply to certain of the notes obtained in confined combustions, it appears inadequate to explain the pronounced metallic knock that causes the real difficulty in engine operation.

Egerton [87] accounts for the knock by the enhanced vibratory combustion near the cylinder walls toward the end of travel of the explosion. Compression waves set up in this way produce the noise.[88] Maxwell and Wheeler [89] found incomplete combustion in the flame front during knocking and noted a vibratory combustion which on reaching the end of the explosion chamber originated a shock wave which caused a violent explosion of the unburned fuel mixture.

Detonation wave theory. Berthelot [90a] and Le Chatelier [90b] discovered that under certain circumstances a detonation wave is set up during the combustion of gases or vapors. Dixon [91] later confirmed the results of these early workers and found that the flame traveled for twelve inches in electrolytic gas before the detonation wave was initiated when the spark was produced three inches from one end of the tube. With a spark at the end this distance became as great as four feet in some cases. Mallard and Le Chatelier [92] noted that the development of the detonation wave was instantaneous and not progressive and that it was characterized by great velocity of movement and intense luminosity. Dixon [93] was also impressed by the sharpness with which the luminosity was set up. Mallard and Le Chatelier [94] found that very large pressures existing for brief periods were developed in the detonation waves and were confirmed by Dixon.

Berthelot and Vieille [95] and Dixon showed the velocity of propagation to be constant and Dixon advanced the theory that the flame had the same speed as sound at the temperature developed in the gas mixture. The investigations of Bunsen, Gouy, and Michelson [96] established the fact that the movement of the zone of explosive reaction in a homogeneous mixture of explosive gases is constant at constant pressure and independent of the mass movement of the gases in which it is propagated. Practical application has been made of this characteristic in cases where a homogeneous, explosive, gas mixture is fed through a tube at a constant rate and ignited.[97]

The speed of a detonation wave has been compared to the mean kinetic speed of the molecules in the burned gases.[98] However, in many instances

[87] Egerton, *Nature* **121**, 876 (1928).
[88] Egerton and Gates, *Proc. Roy. Soc.* **114A**, 402 (1927).
[89] Maxwell and Wheeler, *Ind. Eng. Chem.* **20**, 1041 (1928).
[90] a. Berthelot, *Compt. rend.* **93**, 18 (1881); b. Le Chatelier, *ibid.* **93**, 145 (1881).
[91] Dixon, *Phil. Trans.* **184**, 97 (1893); *Proc. Roy. Soc.* **53A**, 451 (1893).
[92] Mallard and Le Chatelier, *Ann. Mines* (8), **4**, 274 (1883).
[93] Dixon, *Phil. Trans.* **200**, 315 (1902).
[94] Mallard and Le Chatelier, *Ann. chim. phys.* **28**, 289 (1883).
[95] Berthelot and Vieille, *Ann. Chim. Phys.* **28**, 289 (1883).
[96] a. Bunsen, *Ann. physik. Chem.* **17**, 207 (1867); b. Gouy, *Ann. chem. phys.* **5**, 18 (1879); c. Michelson, *Ann. physik. Chem.* **37**, 1 (1889).
[97] a. Stevens, *Ind. Eng. Chem.* **20**, 1018-26 (1928); b. Payman, *ibid.* **20**, 1026-32 (1928); c. Hunn and Brown, *ibid.* **20**, 1032-40 (1928).
[98] Berthelot and Vieille, *Compt. rend.* **93**, 18 (1881); **94**, 149 (1882).

the calculated speeds differ widely from the observed values. The "sound wave theory" proposed by Dixon [99] postulated that the speed of the detonation wave was equal to the speed of sound in the gases at the combustion temperature, but was defective and inadequate to explain all of the facts. In long closed tubes, with no inerts present in the combustible mixture, the velocity of the flame front does approach the velocity of sound, but in short or open tubes the conditions frequently do not permit the attainment of such speeds. Chapman [100] and Jouguet [101] proposed a hydrodynamical theory utilizing equations for the propagation of shock waves in fluids where no chemical changes occurred.

Flame velocity at atmospheric pressure is dependent upon flame temperature and thermal conductivity of the gaseous mixture, i.e., molecular speeds. Increase of pressure appears to have but slight effect in increasing the linear velocity of the flame since it does not alter materially either the temperature or thermal conductivity of the gases. Increase of the initial temperature increases the flame velocity slightly for small increases but more markedly as the ignition temperature is approached.[81, 102]

The high velocity by which the explosion waves move may be accounted for on the basis of the generally accepted chain reaction mechanism for combustion. Such a mechanism explains why the velocity of the interactions may be enormously greater than could be induced by the initially impressed force. The connecting link between the layers of gas through which the explosion moves involves a molecular mechanism. The separate links of the reaction chain are usually exothermic and Lewis has proposed a method for calculating the speed of the explosion wave on the basis of that part of the maximum energy which is energy of translation with the assumption that the evolved energy is divided equally among the several degrees of freedom of the reaction products.[103, 80d] Table XXIV gives a summary of the calculated values with this method as compared to experimental values obtained with a number of reactions.

Morgan,[104] and Maxwell and Wheeler [80, 105] have suggested that these pressure waves are definitely related to engine knock. The high velocity of the wave accompanied by the mass of the gaseous mixtures was assumed sufficient to cause a knock similar to a hammer blow. It was postulated that the more rapid acceleration to the point of detonation necessary in the shorter engine cylinder was caused by the higher temperatures, pressures, and greater turbulence prevailing under such conditions and to the contributory absorption of radiation energy and electrons.[106]

The hypothesis that a true detonation wave is set up, due to ignition by compression of the unburnt charge immediately ahead of a flame front,

[99] Dixon, *Trans. Roy. Soc.* 184, 97 (1883); *J. Chem. Soc.* 97, 665 (1910).
[100] Chapman, *Phil. Mag.* 47, 90 (1899).
[101] Jouguet, *J. de Mathematique*, 1905, 347; 1906, 6.
[102] Garner, *Trans. Faraday Soc.* 22, 252 (1926); *compare* with Ref. 81.
[103] Lewis, *J. Am. Chem. Soc.* 52, 3120 (1930); *compare* with Ref. 80d.
[104] Morgan, *J. Chem. Soc.* 115, 94 (1919).
[105] Maxwell and Wheeler, *J. Inst. Pet. Tech.* 14, 175 (1928).
[106] Maxwell, *J. Inst. Pet. Tech.* 13, 224 (1928); *Fuel Sci. Pract.* 6 (1927), No. 3.

TABLE XXIV.—*Summary of Calculated and Experimental Velocities.*

Explosion	Carrier	Vel. Calc. Meters/sec.	Vel. Obs.[107] Meters/sec.	Deviation Per Cent
$H_2 + O_2$	OH	3160	3532	−10.5
$H_2 + Cl_2$	Cl	1763	1765	− 0.11
$CO + O_2$	O_2	1140	1135	+ 0.44
$C_2N_2 + O_2$	N	2780	2728	+ 1.9
$CH_4 + O_2$	O	2480	2513	− 1.3
$C_2H_4 + O_2$	O	2530	2559	− 1.1
$C_2H_2 + O_2$	O	2947	1941	+ 0.20
$NH_3 + O_2$	O	2435	2390	+ 1.9
$H_2 + N_2O$	OH	2840	>2732	+>3.9
$C_2H_2 + N_2O$	O	2635	2580	+ 2.1
$C_2H_2 + NO$	O	2773 ⎫ 3435 ⎬ 2866 2390 ⎭	2850	+ 0.6
	C			
	N_2			
$C_2H_6 + O_2$	O	2010	2363	−15.0
$CS_2 + O_2$	O_2	1960	1802	+ 8.8
$2O_3 = 3O_2$	O_2	2240	2123	Calc. by Jouguet's theory

is at variance with experimental evidence. Although it is possible that the initial acceleration of the flame may be sufficiently great to develop a detonation wave in certain instances, experiments in closed vessels under conditions comparable to those existing in an engine cylinder do not show flame speeds and accelerations comparable to those of mixtures at the point of detonation. The argument that turbulence may accelerate the flame sufficiently to set up a detonation wave is opposed by the facts that knocking is intensified at slow piston speeds where mixing would be less and by Ricardo's experiments which have shown turbulence to have little effect on the H.U.C.R. of a fuel. Tizard and Pye also found turbulence to increase the temperature necessary for spontaneous ignition.

Increase in the initial pressure of electrolytic gas was found by Dixon [108] to decrease the lag or time necessary for the set up of a detonation wave, a finding confirmed later by Dumanois and Laffitte [109] up to 6.5 atmospheres initial pressure. Dixon found that an increase in the initial temperature decreased the velocity of the detonation wave and Woodbury, Lewis and Canby [110] found high initial temperatures to delay detonation in acetylene, oxygen and nitrogen mixtures.

Using mixtures of pentane and acetylene with oxygen and nitrogen and working at initial pressures of 10 atmospheres and temperatures of 230° C., Egerton and Gates [111] likewise found an increase in initial pressure to decrease the time necessary for detonation to occur up to a certain limit beyond which further increase made little difference. Also, at a given initial pressure increase in initial temperature appeared to retard detonation. One of the well-recognized characteristics of engine operation is

[107] *See* Bone and Townend, "Flame and Combustion in Gases," 1927, pp. 511-518.
[108] Dixon, *Proc. Roy. Soc.* **52A,** 451 (1892).
[109] a. Dumanois and Laffitte, *Compt. rend.* **183,** 284 (1926); b. Laffitte, *Bull. soc. chim.* **41,** 721-45 (1927), review.
[110] Woodbury, Lewis, and Canby, *J. Soc. Auto. Eng.* **8,** 309 (1921).
[111] Egerton and Gates, *Proc. Roy. Soc.* **114A,** 152-60 (1927).

that an increase in the compression ratio, which tends to give higher initial pressures to the air-vapor mixture in the cylinder prior to ignition, increases the tendency to knock. This effect is quite related to the effect of pressure in decreasing the time necessary for the initiation of a detonation wave in an explosive mixture. In the operation of an engine the higher the compression ratio is, the more efficient will be the operation provided knocking does not occur. Hence, it is desired to operate at the highest ratio possible.

In the light of the experimental evidence that has been offered in regard to detonation or explosion waves, it is not clear that a true detonation wave can be set up in the short length of an engine cylinder. It is noteworthy that Woodbury, Lewis and Canby [110] failed to observe detonation in small bombs unless a mixture of oxygen and acetylene was used. The complexity of the later stages of the combustion in an engine cylinder make it difficult to estimate flame temperature and velocity, but it is doubtful if sufficient speed can be attained under such conditions for a true detonation.* Various mechanical details of cylinder construction may influence the knocking tendencies of a given fuel, however, showing that flame propagation may be affected by construction of the reaction vessel.[112]

In attributing the impact of a high velocity, high pressure wave against the cylinder walls as the cause of knock, Midgley [113] derived mathematical equations for the pressure differences existing before and behind the wave. During normal combustion this pressure difference was shown to be insignificant, but with a flame front moving at the velocity of sound the pressure difference becomes enormous and the gas is so highly compressed at the front of the flame as to act as a hammer in striking the cylinder. Hunn and Brown [97c] were of the opinion that these pressure waves were initiated in the inflamed mixture behind the flame front.[114] Egerton and Gates state that "detonation" occurs slightly ahead of the combustion front.[94]

The rate of rise of pressure in a progressive homogeneous reaction cannot be the sole factor determining the tendency of a fuel to knock. Brown and Watkins [115] determined the rate of the pressure rise in a number of progressive homogeneous reactions and came to the following conclusions:

The rate of pressure increase (1) increases with the molecular weight of normal paraffin hydrocarbons; (2) varies inversely with the number of methyl groups attached to an aromatic nucleus; (3) is approximately the same for benzene and n-octane, toluene and n-heptane, xylene and n-hexane; (4) is about the same for the higher alcohols as for the corresponding hydrocarbon; (5) is very rapid for ethyl ether. Table XXV summarizes the results of their work.

* *See* Ref. 84.
[112] *See also* Maxwell, *J. Inst. Pet. Tech.* **13**, 224 (1927).
[113] Midgley, *J. Soc. Auto. Eng.* **10**, 361 (1922).
[114] Dixon, *Trans. Roy. Soc.* **200A**, 319 (1903); *J. Soc. Auto. Eng.* **9**, 237 (1921).
[115] Brown and Watkins, *Ind. Eng. Chem.* **19**, 280-5 (1927).

TABLE XXV.—*Rate of Pressure Rise in Progressive Homogeneous Reaction.*

Fuel	Max. dP/dt lbs./sq. ins.	Ave. $\Delta P/\Delta t$ lbs./sq. ins.
n-Hexane	47500	34600
n-Heptane	61500	37400
n-Octane	63700	40550
Benzene	63000	43400
Toluene	56500	38200
Xylene	47000	35500
Methanol	52000	36100
Ethanol	39500	30900
Amyl alcohol	48000	33700
Ethyl ether	>200000	48400
Toluene	56125 (ave. of 4)	38175 (ave. of 4)

From a study of the effect of initial temperature on the rate of rise of pressure Brown, Leslie and Hunn [110] arrived at the same conclusion. Fenning's [117] results showing that the rate of flame propagation is greater with benzene-air than with hexane- or gasoline-air mixtures also supports the proposal that tendency to knock cannot be measured by flame speeds.

Only in extreme cases is knocking caused by a true detonation wave. [88] Brown and Watkins state that the detonation wave as recognized in progressive homogeneous reactions is not the cause of knock. [118]

Self-ignition theory. A distinction must be made between knock and self-ignition in the absence of spark which may occur with a knock. Thus, methanol and carbon disulfide self-ignite but do not knock while kerosene causes a knock without showing any tendency to self-ignite. Ricardo [119] distinguished between preignition and "pinking" or knocking. His theory amounts to a practical exposition of knocking. An explosion wave is set up in the burning gaseous mixture when the rapidity of combustion of that portion of the mixture first ignited, is such that by expansion it compresses before it the unburnt portion. When the rate of temperature rise due to compression by the burning portion of the fuel, exceeds the rate at which it can dissipate heat by conduction, etc., the remaining portion ignites simultaneously throughout. This sudden ignition sets up an explosion wave which acts as a hammer on the cylinder walls and causes the knock. This theory assumes a self-ignition tendency for the fuel, and implies [120] a tendency to knock proportional to the spontaneous ignition temperature of the fuel. [121]

Woodbury, Lewis and Canby [110] were not able to detonate ethyl ether-air in their small bomb apparatus, although ether is recognized to have bad knocking characteristics when used in an engine. However, they observed

[110] Brown, Leslie and Hunn, *Ind. Eng. Chem.* 17, 397 (1925).
[117] Fenning, *Aero. Res. Comm. Rept.* No. 979, B 15.
[118] Brown and Watkins, *Ind. Eng. Chem.* 19, 363 (1927).
[119] Ricardo, *Proc. N. E. Coast Inst. Eng. and Ship.* 34, 316 (1918). *Compare* (112) Maxwell, *loc. cit.*
[120] Kelly, *J. Inst. Pet. Tech.* 13, 101 (1927) review.
[121] a. Ricardo, *Auto. Eng.* (*England*) 11, 92 (1921); b. Ricardo, *J. Soc. Auto. Eng.* 10, 308 (1922); c. Kettering, *ibid.* 5, 1898 (1919).

"auto-ignition" ahead of the flame front in certain cases. Under such conditions the photographs showed rapid vibrations in the burning mixture and a loud knock was audible. The experimental evidence obtained by these workers supports the theory that knocking is due to the sudden ignition of the unburned charge rather than to the propagation of a high temperature, high pressure detonation wave through the combustible mixture.

Explosions of hexane-air mixtures at initial temperatures of 200° to 230° C. and pressures of 48.2 to 120.5 pounds per square inch showed violent vibration of pressure toward the end of the combustion period whenever the initial temperatures and pressures were sufficiently high.* The slow pressure rise obtained in the combustion under conditions approximating those prevailing in engine operation seem to contraindicate detonation. Rather an increase in the rate of burning by spontaneous combustion and the setting up of vibrations by multiple flames produced in this manner seems to be a better explanation of the loud knocks obtained. Petavel [122] observed similar phenomena in the explosion of coal gas-air mixtures at an initial pressure of 70 atmospheres. Calculation of the temperature of the mixture at the point where the pressure showed a sudden increase gave values approximating that for spontaneous ignition of the mixture. Fenning arrived at similar conclusions in regard to the hexane-air mixtures.

Tizard and Pye [123] had similar views on the cause of knocking and studied the ignition temperatures of fuels by adiabatic compression methods. The pressure record obtained by them in this work show a lag subsequent to arrest of the moving piston used to compress the charge and prior to the increase of pressure due to inflammation. Tizard's diagrams show a sharp rise in pressure subsequent to this lag period, corresponding to a sudden ignition of the gaseous fuel. This lag period decreased with increase of pressure and was different for the various fuels used in the work. Tizard was of the opinion that the temperature coefficient of the reaction as shown by this lag is an important factor in determining the knocking characteristics of a fuel. Thus, heptane and ethyl ether knock badly in an engine and have short lag periods. Carbon disulfide raised the H.U.C.R.,** when added to gasoline and also had a long lag period. A long lag period permits normal combustion and prevents spontaneous ignition.

Uncertainty shrouds the events subsequent to spontaneous ignition, but in the experimental work with carbon disulfide and oxygen mixtures the flame travel through the tube never reached speeds comparable to detonation.

* *Compare* Ref. 117; *also* Ref. 112.
[122] Petavel, *Phil. Mag.* 3, 461 (1902).
[123] a. Tizard, *Proc. N. E. Coast Inst. Eng. and Ship.* 37, 381 (1921); b. Tizard and Pye, *Phil. Mag.* (6) 44, 79 (1922); (7) 1, 1094 (1926).
** The highest ratio that may be used with a fuel before knocking takes place, is called the highest useful compression ratio (H.U.C.R.) for that fuel. Fuels may, hence, be rated by their H.U.C.R. to show tendency to knock, i.e. the higher the H.U.C.R. the less the tendency to knock.

Many attempts [97, 106, 110, 124] have been made to obtain evidence for the support of the various theory regarding knocking by photographing the explosion of inflammable mixtures in fixed volume bombs, while making a simultaneous pressure record. The photographic data obtained in this way showed that the combustion phenomena giving rise to a knock took place during the latter part of the explosion, and indicated that the spontaneous ignition of the unburnt portion of the charge ahead of the flame front caused a sudden rise in pressure which produced the knocking noise. It was noted that the combustion in the moving flame front was apparently not complete even in "knocking" operation and an after glow occurred. It was supposed that the sudden ignition of the unburned charge generated a shock wave which caused the completion of combustion throughout the cylinder at once. In non-knocking explosions the combustion reactions were found to be continuous and long continued after the flame front had passed through the mixture.

It was, however, not possible to translate such data directly to engine operation and the need for following the combustion in an actual engine cylinder by means of chemical analysis, photographs, and pressure records was recognized.[125] The data obtained from the operation of such a specially fitted engine have shown that a comparatively narrow combustion wave moves across the cylinder from the spark plug at a speed which increases with the engine speed. Combustion is complete in this moving zone. With an engine speed of 800 r.p.m. this combustion zone moved with a speed of 60 to 74 ft. per sec. when benzene was the fuel and with a speed of 80 ft. per sec. when a mixture of equal parts by volume of benzene and gasoline was used. The phenomenon of knocking is definitely associated with the combustion of the last portion of the mixture to ignite and is due to a manyfold increase in the rate of combustion of this last portion. Non-knocking operation of an engine is characterized by the absence of this sudden increase in combustion rate.

Depending on the conditions of operation the ignition of this last portion of the fuel-air mixture may occur in any one of several different ways. It is possible that spontaneous or self-ignition of the charge ahead of the flame front may occur at one or more points and that the flame then spreads rapidly throughout the chamber. The entire unburned charge may ignite at once instead of at several points ahead of the normal combustion zone. Again, the normal zone of combustion moving across the cylinder may suddenly increase in speed toward the end of its travel. The fact that evidence to show that each of these three types of combustion may occur during knocking operation has been obtained indicates that more than one factor may be accountable. A pre-ignition glow observed in the

[124] a. Brown and Carr, *Ind. Eng. Chem.* 21, 1071 (1929); b. Brown and Souders, *ibid.*, 21, 1261 (1929); c. Maxwell and Wheeler, *ibid.* 20, 1041-4 (1928); d. Kirkby and Wheeler, *J. Chem. Soc.* 130, 3203 (1928).
[125] a. Withrow, Lovell, and Boyd, *Ind. Eng. Chem.* 22, 945-51 (1930); b. Withrow, and Boyd, *Pet. Div. Am. Chem. Soc.* April, 1931, Indianapolis, Ind.

unburned charge prior to the sudden inflammation gives the only clue as to the possible mechanism.

In the face of a lack of analytical evidence it is hazardous to postulate just what is the mechanism of the sudden inflammation of the latter portion of the charge during knocking operation of an engine. The addition of sufficient lead tetraethyl to the gasoline to stop knocking was found to have no effect on the progress of the narrow normal combustion zone across the cylinder until the latter part of travel was reached, at which point the sudden increase in rate was suppressed.

From the evidence it may be concluded that a detonation wave will not be set up in an engine cylinder in a manner similar to that obtained in long tubes. Although a close relationship appears to exist between ignition by compression and the occurrence of knocking in an engine cylinder, the conditions of operation are different and further elucidation is needed. Thus, while spontaneous ignition can account for the facts that knocking occurs more readily with paraffins than with aromatic hydrocarbons since the ignition temperatures of the former are lower, that it occurs with higher molecular weight hydrocarbons more readily than with lower molecular weight ones for the same reason and because flame temperature increases with molecular weight, and that factors reducing explosion temperature reduce the tendency to knock, it does not directly account for the fact that knocking is greatest with mixtures developing the most power, whereas variation in mixture composition has little effect on spontaneous ignition.[80b, 128b] Data on the effect of antiknock dopes on ignition temperatures also fails to support the spontaneous ignition theory.

Radiation and ionization. The work with bombs and engines has indicated that small amounts of antiknock dopes eliminated the shock wave in combustions of explosive mixtures and induce a continuous combustion in the wake of the flame front. It has also shown that during knocking combustion a partial burning outruns the remainder and causes a violent liberation of energy during some portion of the cycle.*

Studies of flame radiation during combustion have supported these findings. Thus, Clark and Henne [128, 81] found that during knocking operation of an engine, the spectrum of the first quarter of the combustion period was intense and extended into the ultra-violet region, and that of the succeeding portion greatly diminished in energy. A great liberation of energy during the first quarter of the stroke was thus indicated. The addition of lead tetraethyl caused the spectrum to return to the proportions of non-knocking operation. The appearance of lead lines during the early part of the combustion only, indicated to these workers that the antiknock functioned near the start of combustion. The action of the dope is thus to slow down reaction when it becomes over vigorous. This

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* *Cf.* Rassweiler and Withrow, *Ind. Eng. Chem.* **24**, 528 (1932); Withrow and Rassweiler, *ibid.* **23**, 769 (1931).
    128 a. Clark and Henne, *Compt. rend.* **184**, 26 (1927); *J. Soc. Auto. Eng.* **20**, 264 (1927); b. Clark, *ibid.* **23**, 167 (1928).

conclusion is at variance with the recent findings of Withrow and Boyd, who believe that the events giving rise to knocking take place only during the latter portion of the combustion period. It is probable that the intense liberation of light energy during knocking operation is an accompaniment rather than a cause of the phenomenon.[127]

"Activation" of the unburned portion of the fuel-air mixture by radiant energy is dependent upon the density of the gaseous mass since absorption of such energy is a function of density. The absorption of radiation supposedly tends to decompose the hydrocarbons into hydrogen, or lighter constituents which then burn with a higher velocity to generate a knock producing pressure wave. The influence of hydrogen in causing knocking in this way is based on the old free hydrogen theory.

Lind [128] likewise states that absolute density may be a factor in the cause or prevention of knocking, drawing an analogy to the case of hydrogen and oxygen reaction under the influence of alpha particles. Higher density or greater stopping power of the reacting mixture gives greater velocity of reaction.

EFFECTS PRODUCED BY ANTIKNOCK DOPES

Effect on knock. In order to eliminate the knock which occurs with some fuels in the operation of internal combustion engines it is necessary to add only very small amounts of the organometallic compounds such as lead tetraethyl, nickel carbonyl, or iron carbonyl. Such substances have, hence, been looked upon as the premier antiknock dopes. In the case of the organic amines such as aniline, toluidine, and methyl aniline amounts up to 10 per cent by volume of the fuel are required before the desired effects are obtained. While the aromatic hydrocarbons, naphthenes, and alcohols are not strictly antiknock dopes, gasolines that are high in either are more resistant to knocking. As an example an addition of 50 per cent of benzene to a gasoline is necessary before knocking is suppressed to the same extent caused by a 5 per cent toluidine addition. Many oxygenated organic compounds as amyl and butyl nitrites, organic peroxides as well as certain elements as bromine act as knock inducers.

The results of Sims and Mardle's work indicate that iron and nickel carbonyl are more efficient than lead tetraethyl. A comparison of the three compounds on the basis of equal amounts of metal per unit of fuel

TABLE XXVI.—*Comparison of Efficiency of Antiknock Dopes.*

Compound	Wt. Metal gms./liter	Wt. Compound gms./liter	H.U.C.R.	Increase in H.U.C.R. Per Cent
Gasoline	—	—	4.6	0
Gasoline + Pb(C_2H_5)$_4$	2.0	3.2	6.45	40
Gasoline + Ni(CO)$_4$	2.0	5.8	6.8	48
Gasoline + Fe(CO)$_5$	2.0	7.2	7.41	61

[127] a. "Symposium on Gaseous Reactions," Faraday Soc. (1926); b. Mardles, *Nature* 121, 424-7 (1928).
[128] Lind, *Trans. Am. Electrochem. Soc.* 44, 63 (1923); *J. Am. Chem. Soc.* 44, 531 (1919).

shows the basis for the conclusion. The use of the carbonyls of iron and nickel has been largely confined to continental Europe, however. The I. G. Farbenindustrie at one time marketed "Motalin," a gasoline containing 0.2 per cent of iron carbonyl but has subsequently withdrawn the fuel from the market. For reasons other than high efficiency alone, tetraethyl lead has remained the premier antiknock compound and is used throughout the world.[129]

The relative efficiency of a number of antiknock dopes in suppressing knocking of a kerosene is shown by Table XXVII.

TABLE XXVII.—*Relative Effect of Various Dopes in Suppressing the Knock of Kerosene.*[130] *

Antiknock Compound	Volume in Kerosene Per Cent	Mols Theoretical Fuel-Air per Mol of Dope to Give Standard Knock
Benzene	25.0	150
Ethyl iodide	1.6	2150
Xylidine	2.0	2600
Tin tetraethyl	1.2	7100
Selenium diethyl	0.4	11750
Tellurium diethyl	0.1	50000
Lead tetraethyl	0.04	215000

Egerton and Gates have arranged the most effective antiknocks in the order of their effectiveness in suppressing knocking as: iron carbonyl, lead tetraethyl, nickel carbonyl, aniline, m-xylidine, and toluene, and rank them 600, 400, 160, 11, 12, and 1, respectively, in effectiveness.[48]

Studies [61, 84, 131] of the various organo-metallic compounds have shown that only those of metals which are capable of ready oxidation are effective. Metals capable of existing in a number of states of oxidation are particularly effective. Organic compounds with the metal atom linked through an oxygen atom are not effective in stopping knock.

The fact that the colloidal metal sols which have been used in some of the work were found to be highly pyrophoric and that colloidal sols of carbon, silver, or gold were without effect in raising the H.U.C.R. has added weight to the conclusion that to be effective as an antiknock the metal must be readily oxidized and capable of existing as an oxide under combustion conditions. Compounds of such metals as are decomposed at temperatures below 300° C. should have an effect in suppressing knock. In general, the effectiveness of organo-metallic compounds depends upon the proportion of the metal which is free and uncombined at the temperature of oxidation. Thus, aryl compounds are more stable and less effective than alkyl derivatives of the metals.

[129] a. Mond, *J. Soc. Chem. Ind.* 49, 287T (1930), carbonyls; b. Frydlender, *Rev. prod. chim.* 31, 361-4 (1928). (mfg. and props. of $Fe(CO)_5 + PbEt_4$); c. Edgar, *Oil and Gas J.* 27, 162-4 (1928), anti-knock.
[130] Midgley and Boyd, *Ind. Eng. Chem.* 14, 894 (1923).
* Average molecular weight of kerosene assumed = 184.
[131] Sims and Mardles, *Trans. Faraday Soc.* 22, 363 (1926).

Also, the higher alkyl derivatives of lead are not as efficient as the tetraethyl compound. Thus, the butyl triethyl lead derivatives are only about 85 per cent as effective in suppressing knock as is the tetraethyl compound.[182] The dibutyl diphenyl lead compounds range from 33 to 45 per cent as good as lead tetraethyl. While the various quadrivalent derivatives of lead show varying degrees of antiknock action, the bivalent derivatives with a few exceptions show no action.

Tests were made on various organic derivatives of different metals by Sims and Mardles but none of these had any marked action toward inhibiting detonation in an engine. These compounds included aluminum, cobalt and mercury naphthyls; copper and cerium xylyls; copper, cobalt, and gold oleates; chromium, iron, lead, mercury, tungsten and uranium phenyls. Evidently considerable importance must be attached to the organic group comprising the organo-metallic compounds probably because of the decomposition characteristics.

The antiknock property of a particular compound, however, has been considered to be primarily a function of the element rather than of the organic groups attached to it. A comparison of the knock suppressing capacities of the ethyl compounds of iodine, selenium, and tellurium with the phenyl compounds show the direction and order of the magnitude of the effects produced to be in the same direction for each element. The aryl compounds are, nevertheless, not as effective as the alkyl.[183] The lighter elements of a periodic group behave as pro-detonants and the heavier members are anti-detonants, viz., chlorine and bromine are pro-detonants whereas iodine is a knock suppressor.[130, 134] Two forms of the same element may have different actions, tervalent antimony is an anti-detonant and pentavalent antimony a pro-detonant. In the case of the nitrogen atom, the effect of the compound on knocking cannot be as independent of the substituents as in the case of the metal atoms, and the effects of the other atoms in the molecule must be considered.[185]

Taylor's experiments [136] on the decomposition of metal alkyls led him to believe that the active alkyl groups, released by decomposition of the compounds, functioned in the same way as the active metal atoms. Experiments have shown that the presence of hydrogen atoms induces oxidation of ethylene at room temperature. The theory is advanced that the free alkyl radicals act in a manner similar to hydrogen atoms or metal fogs, i.e., as active oxidation centers producing a slow homogeneous combustion of fuel. This action of free radicals may account for the effects of non-metallic knock suppressors as aniline, toluidine, etc.

Among the non-metallic organic compounds that have been found effective to various extents as antiknocks the amines are perhaps the most important. None of them can compare with the metallic compounds,

[182] Gilman, Sweeney and Robinson, *Chimie et Industrie* 24, 55 (1930).
[183] Midgley, *Ind. Eng. Chem.* 15, 421 (1923).
[184] Wendt and Grimm, *Ind. Eng. Chem.* 16, 890 (1924).
[185] Moureu and Dufraisse, *Compt. rend.* 182, 949-51 (1926).
[136] Taylor, *Trans. Faraday Soc.* 21, 560-8 (1926).

however. Aniline is about 1/40 as effective as lead tetraethyl. Mono-methyl aniline is slightly more effective than aniline and dimethyl aniline less effective. Quinoline, pyridine, and carbylamine are ineffective com-pared to aniline. Meta-xylidine is about the most effective of the aryl-amines being 1/30 as good as lead tetraethyl. In general, meta compounds are more effective than the corresponding ortho and para derivatives. Diethylamine is less effective than diphenylamine, contrary to the case when a metal atom is present. Other than the aryl amines and other nitrogen compounds about the only organic substances effective as antiknocks are ethyl iodide, quinone, cresol, phenol, ethylene dibromide, and diphenyl oxide, none of which are as good as aniline. Water has even been reported to have a favorable effect in retarding knock.[137] Aldehydes, organic acids, nitro compounds, nitrates, nitrites, and most of the halogen compounds promote knocking.

The theories that have been advanced to the effect that the decompo-sition products of the antiknock dopes and not the compounds themselves are the effective centers of the action has been tested by the use of metallic colloids, prepared in various ways, in the fuels by which engines were operated. The work on colloidal metal sols has been based on the theory that knocking is due to the spontaneous ignition of the unburned charge in an engine cylinder. By acting as catalysts for combustion these sub-stances insure a slow, homogeneous combustion rather than a detonation.

Some of the first work [138] showed that free metallic particles suspended in the combustion zone of an internal combustion engine cylinder do not have a measurable effect in suppressing detonation. Olin, Read, and Goos used a motorcycle engine, cooled by a fan and operating at 1400 r.p.m. for test purposes. The data from the operation with different fuel and fuel-colloid mixtures were interpreted by plotting cylinder temperature against horse power output. Nickel and lead colloids were prepared by decom-position of the organic derivatives. Although the colloidal metals had no apparent effect on the combustion, the theory that antiknocks were active through the products of decomposition was not considered disproved since such particles formed *in situ* would be in a much higher state of activity and, hence, much more effective in suppressing detonation.

The results obtained by Sims and Mardles,[139] however, showed that freshly prepared colloidal metal sols in gasoline are just as effective as the organo-metallic compounds. The colloidal dispersions were prepared by heating the carbonyls or ethides in gasoline to which a small amount of rubber had been added for stabilization of the sols. The dispersions of nickel, lead, and iron were found to be as effective as the organic deriva-tives from which they had been prepared in raising the highest useful compression ratio (H.U.C.R.) at which the engine could operate with the fuel used. A summary of the results is shown by Table XXVIII.

[137] Hobbs and Fast, *Mich. Expt. Sta. Bull.* No. 31, 15 pp. (1930).
[138] Olin, Read, and Goos, *Ind. Eng. Chem.* 18, 1316-8 (1926).
[139] Sims and Mardles, *Engineering* 121, 774 (1926).

TABLE XXVIII.—*Effect of Colloidal Metals in Raising the H.U.C.R. of Gasoline.*

Metal	Method of Preparation	Increase in H.U.C.R. Per Cent
Nickel	0.5 per cent $Ni(CO)_4$ therm. decomp. hexane	40.5
Nickel	0.5 per cent $Ni(CO)_4$ therm. decomp. gasoline	41.5
Nickel	0.5 per cent $Ni(CO)_4$ not decomposed	38.0
Lead	$Pb(C_2H_5)_4$ therm. decomp. in petroleum jelly and naphthalene, some lost	33.8
Lead	$Pb(C_2H_5)_4$ control for above	35.0
Lead	$Pb(C_2H_5)_4$ therm. decomp. in bromonaphthalene at b.p., some lost	19.6
Lead	$Pb(C_2H_5)_4$ control for above	25.5
Lead	$Pb(C_2H_5)_4$ 3 cc. in gasoline 200 cc. decomp. high freq. spark 10 mins.	31.6
Lead	$Pb(C_2H_5)_4$ control for above	33.0
Iron	$Fe(CO)_5$ therm. decomp. boiling naphthalene 25 mins.	42.0
Iron	Same for 40 mins.	45.4
Iron	$Fe(CO)_5$ control for above	41.0
Iron	$Fe(CO)_5$ therm. decomp. in bromonaphthalene some interaction	7.0
Iron	$Fe(CO)_5$ control for above	11.4
Iron	$Fe(CO)_5$ spark decomp. for 7 mins. in gasoline soln. 25 per cent decomp.	23.0
Iron	$Fe(CO)_5$ control for above	24.4

The results of Olin and Jebens [140] shown in Table XXIX do not harmonize with the results of either of the two preceding sets of experiments. A successive decrease in useful compression ratio is shown by successive increases in temperature of decomposition of the organo-metallic compound. The conditions for maintaining stability of the metallic sols were comparable to those of Sims and Mardles. Hence, it appears that Sims and Mardles may have erred in not obtaining as complete a decomposition of the organic compounds as would be necessary to show effectively the action of the colloidal metals.

TABLE XXIX.—*Anti-knock Properties of Metal Colloids Prepared at Different Temperatures.*

Fuel	H.U.C.R.	Increase in H.U.C.R. Per Cent	Initial Conc. of Anti-knock cc./liter
Gasoline	4.37	—	0
Gasoline + $Ni(CO)_4$	4.70	7.54	5.501
Gasoline + $Ni(CO)_4$ heated 69° C.	4.63	5.94	5.501
Gasoline + $Ni(CO)_4$ heated 77° C.	4.56	4.35	5.501
Gasoline + $Ni(CO)_4$ heated 85° C.	4.41	0.92	5.501
Gasoline	4.43	—	0
Gasoline + $Pb(C_2H_5)_4$	5.02	13.3	1.0
Gasoline + $Pb(C_2H_5)_4$ heated 250° C.	4.76	7.5	1.0
Gasoline + $Pb(C_2H_5)_4$ heated 275° C.	4.55	2.7	1.0
Gasoline + $Pb(C_2H_5)_4$ heated 300° C.	4.44	0.0	1.0

Effect on ignition temperature and rate of reaction. The consensus of opinion, in general, is that knock inducers lower and knock suppressors raise the ignition temperature of a fuel,[63a, 141] but certain

[140] Olin and Jebens, *Ind. Eng. Chem.* 21, 43 (1929).
[141] Bennett and Mardles. *J. Chem. Soc.* 1927. 3155: 1928. 870.

contradictions exist in regard to this opinion. Some authors [68b, 68d] believe that the effect of knock suppressors as lead tetraethyl is to raise or lower the auto-ignition temperature of either pure substances or gasolines toward an optimum ignition temperature corresponding to a decreased knock tendency.[142] Midgley [143] evolved the high velocity, high pressure wave theory and did not believe antiknocks affected the spontaneous ignition of fuels. Ormondy and Craven examined the effect of anti-knocks in Moore's apparatus and found results contrary to their expectations. They concluded that antiknocks did not affect ignition temperatures under these conditions to the extent that they do in an engine.[68c] Ricardo [144] states that antiknocks appear to have no effect on flame propagation but affect the self-ignition temperatures of fuels. There is, however, a considerable mass of experimental evidence which supports the contention that antiknock dopes are effective by raising ignition temperatures.

Using a special iron cup apparatus Weerman [62] found a very great difference between the temperatures of treated and untreated gasoline. The results of some of this work are shown in Table XXX in the form of oxygen consumption per gram of gasoline at given temperatures.

TABLE XXX.—*Influence of Dopes on Consumption of Oxygen by Gasoline.*

Fuel	Temp. ° C.	Cc. O_2/Gm. Gasoline
Gasoline	320	330
	390	360
Gasoline plus 4 gm. $Si(C_2H_5)_4$ per liter	320	370
	390	390
Gasoline plus 2 gm. $Se(C_2H_5)_2$ per liter..........	320	195
	400	185
	450	165
	470	185
	500	255
Gasoline plus 2 gm. $Pb(C_2H_5)_4$ per liter	320	205
	400	215
	450	285

In the case of gasoline plus an antiknock agent the consumption of oxygen is less at the same temperature than with gasoline alone, showing that these compounds have the capacity to retard oxidation. And since the ignition temperature is dependent on the relation between the speed at which heat is developed and that at which it is lost these compounds should increase the ignition temperature of a fuel.

The results obtained by Weerman with a number of other compounds are shown in Table XXXI. Apparently, only those elements are active which are capable of producing oxides which can be reduced under the conditions existing in an operating engine cylinder or which can exist in more than one degree of oxidation. Also, the compounds to be effective

[142] Masson and Hamilton, *Ind. Eng. Chem.* 21, 544 (1929).
[143] Midgley, *Ind. Eng. Chem.* 14, 894 (1922).
[144] Ricardo, *Inst. Auto. Eng. Rept. Motor Fuels Comm.* 28, p. 327, part I.

must be volatile at conditions which will insure complete dispersion in the reacting gases.

TABLE XXXI.—*Effect of Compounds on the Self-Ignition Temperature of Gasoline (Weerman).*[62]

S.I.T. Gasoline = 335° C.

Dope	Gms./Liter	S.I.T. ° C.	Difference ° C.
$Pb(C_2H_5)_4$	0.5	440	105
	1.0	465	130
$Fe(CO)_5$	2.9	505	170
$Ni(CO)_4$	1.0	395	60
$Hg(C_2H_5)_2$	2.0	340	5
$Se(C_2H_5)_2$	0.5	450	115
	1.0	475	140
$Te(C_2H_5)_2$	1.0	390	55
	2.0	405	70
$B(C_2H_5)_3$	4.0	325	—10
$Cr(CO)$	4.0	415	80
$Sn(C_2H_5)_4$	2.0	410	75
	4.0	445	110
$Zn(C_2H_5)_2$	10.0	325	—10
$Al(C_2H_5)_3$	2.0	325	—10
$Bi(C_6H_5)_3$	1.0	420	85
	2.0	440	105
$Si(C_2H_5)_4$	4.0	325	—10
Cobalt acetylacetone	2.0	335	0
Manganese acetylacetone	2.0	335	0
Iron acetylacetone	2.0	335	0
Ethyl mercaptan	2.0	335	0
Ethyl sulfide	2.0	335	0
Ethyl iodide	10.0	395	60
Aniline	5.0	400	65
	10.0	415	80
Acetyl diphenylamine	5.0	335	0
Diphenylamine	10.0	425	90
	5.0	410	75
p-Phenitidine	5.0	400	65
	10.0	440	105
Pyramidon	5.0	345	10
Dimethyl 3,5-pyrazole...........	5.0	335	0

By comparison with Weerman's results Egerton and Gates obtained even higher rises in ignition temperature relative to the amount of anti-knock dope used.[43] Some of their results with both metallic and non-metallic dopes are shown in Table XXXII. A modified Moore apparatus was used.

One mol of lead tetraethyl was found to be as effective as 70 of aniline in raising the ignition temperature of gasoline. Organic substances which were effective at concentrations of one per cent included amines, amides, imides, phenols, and quinone. The general behavior of organic antiknocks on hydrocarbons, aldehydes, etc., seemed to be similar to that of metallic compounds in decreasing the oxidation as measured by the oxygen and carbon dioxide content of the gases and the composition of the products

TABLE XXXII.—*Rise of Ignition Temperature of Gasoline by Antiknock Dopes.*

		Rise in I.T. in ° C. Caused by Addition of			
Substance	0.1%	1%	2%	5%	10%
Aniline		30	60	100	110
Toluidine		35			
Xylidine		40	65	100	110
α-Naphthylamine		20			
Dimethyl aniline		10	20		
Diphenyl amine		50	90		
Quinone		30	35		
Acetone		5	10	40	60
Benzene				30	20
Selenium diethyl	140				
Iron carbonyl	130				
Bismuth triethyl	120				
Lead tetraethyl	90				
Nickel carbonyl	40				
Tellurium diethyl	55				
(Tin tetraethyl	50)				
Bismuth triphenyl	42				

found during the operation of an engine. No substance was found to be effective in the engine as an antiknock that was not effective in raising the ignition temperature in the Moore apparatus cup, but the reverse was not found to hold.

By measuring the current in the hot wire used to ignite mixtures of doped and undoped fuels with air, Boord and Schaad [145] were able to differentiate between the effect of knock inducers and suppressors. Knock suppressors as lead tetraethyl, lead tetramethyl, selenium diethyl, aniline used with toluene, isoamyl acetate and kerosene; ethyl iodide used with toluene; phenyl iodide used with diethyl fumarate and diethyl maleate, all increased the filament current necessary for ignition from 0.5 to 2.0 amperes above normal. Knock inducers as isoamyl nitrite with toluene, isoamyl acetate and kerosene; propyl nitrite with toluene; nitrobenzene with isoamyl acetate, kerosene, and diethyl fumarate, all lowered the current required in the hot wire for ignition. These results were not checked by Ormandy and Craven's work with n-heptane and lead tetraethyl. However, these workers used the Moore cup apparatus which is subject to considerable variation at the hands of different investigators. Masson and Hamilton, however, found the autoignition temperature of n-heptane to be raised from 450° to 545° C. by the action of lead tetraethyl. This latter finding is supported by the results obtained by Layng and Youker,[4a] who observed that the slow oxidation of heptane in the gas phase at 160° C. was inhibited by lead tetraethyl. Oxidation of hexane at 350° to 500° C. is also less in the presence of small amounts of lead tetraethyl, iron carbonyl, or nickel carbonyl.[146]

Butkov [147] found that n-heptane heated in a bomb at 230° C. and under

[145] Boord and Schaad, *Ind. Eng. Chem.* 21, 756 (1929).
[146] Callendar, *Engineering* 123, 182 (1927).
[147] Butkov, *Podsl. Trav. 4*, 162 (1928).

three atmospheres oxygen pressure yielded carbon dioxide six times more rapidly than when two per cent of aniline was present. Similar results were obtained by Dumanois and Mondain-Monval,[74] who worked with a steel bomb which was heated from 20° to 300° C. during an experiment and showed that with super-atmospheric pressures of air the oxidation of pentane mixtures richer than theoretical was inhibited by 0.11 per cent of lead tetraethyl and the spontaneous ignition temperature was increased by 10° C. A fuel doped with an antiknock is much less easily oxidized than ordinary fuel during the compression stroke of an operating engine.[43]

Lovell and Coleman [148] showed by analyzing combustion products that gasoline burns more rapidly in the presence of knock inducers and that lead tetraethyl added to the mixture brings the rate of burning back to normal.

With pure oxygen the effect of lead tetraethyl on gasoline is slight.[43, 68c, 149] However, Lewis [150] found that isopentane heated with oxygen in a glass apparatus to a temperature below the ignition point was more resistant to oxidation by the addition of one per cent of lead tetraethyl.

In general, the effects of antiknock dopes on the ignition temperatures of combustibles other than the normal aliphatic hydrocarbons show wide variations. Normal alcohols are but little affected whereas the temperature required for aldehydes to ignite is greatly raised. Benzene which has a high ignition temperature is affected but slightly. Isohexane is affected less than n-hexane.[48] Table XXXIII shows the effect of lead tetraethyl on the ignition temperatures of a number of hydrocarbons.

TABLE XXXIII.[69c]—*Change in Ignition Temperature by Lead Tetraethyl.*

Ignition was in an iron crucible in air with 0.25 per cent by volume of dope.

Hydrocarbon	Ignition Temperature ° C.	Temperature Increase ° C.
Benzene	690	18
Cyclohexane	535	27
Methylcyclohexane	470	92
Pentane (1)	515	75
Pentane (2)	540	87
Isohexane	525	46
Heptane	430	83
Shell Gasoline	460	82

On the basis of the spontaneous ignition theory and the high pressure high velocity wave theory, Midgely and Boyd [180] conclude that although it is difficult to explain the action of antiknocks on the basis of auto-ignition, the experimental evidence fits the reduction in reaction velocity theory. Table XXXIV shows results obtained from a study of the effect

[148] Lovell and Coleman with Boyd, *Ind. Eng. Chem.* 19, 376 (1927).
[149] Tanaka and Nagai, *Proc. Imp. Acad. Tokio* 2, 221 (1926).

caused by small amounts of antiknock compounds on the speed of combustion.

TABLE XXXIV.—*Effect of Different Substances on Reaction Velocity.*[151, 130]

Element	Compound	Effect on Reaction Velocity
Iodine	element	retards
Bromine	element	accelerates
Oxygen	element	accelerates
Oxygen	ethyl nitrate or nitrite	accelerates
Nitrogen	aniline	retards
Selenium	$Se(C_2H_5)_2$	retards
Tellurium	$Te(C_2H_5)_2$	retards
Tin	$Sn(C_2H_5)_4$	retards
Lead	$Pb(C_2H_5)_4$	retards

Since it had been shown that under certain conditions, antiknock compounds could be made to affect the ignition temperature of fuels used in internal combustion engines, and because of the controversies that existed in regard to the effect of colloidally dispersed metals in suppressing engine knock, Egerton and Gates [48] performed experiments to determine the effect of colloidal metals on the ignition temperature. The cup method of Moore [152] was used to obtain the data and the metals were dispersed by means of an electric arc in an inert gas atmosphere. The results of these experiments show that thorium, potassium, lead, iron, nickel, manganese, bismuth, selenium, tellurium, sodium, cadmium, calcium, antimony were effective in raising the ignition temperature of gasoline; and that copper, zinc, and silver were slightly effective in this way. The elements of aluminum, magnesium, mercury, iodine, phosphorus, and gold were without effect on the ignition temperature. Iron, nickel, tin, cerium, and vanadium gave doubtful results by the arc method. Titanium, zirconium, thorium, scandium, tantalum, tungsten, molybdenum, chromium, cobalt, platinum metals, and uranium were difficult to test by the arc method. Although they were not tested, lithium, cesium, rubidium, barium, strontium, gallium, and indium would probably be effective and silicon, boron, arsenic, germanium and beryllium would probably not be effective in raising ignition temperature.

From these results it may be concluded that only oxidizable metals influence the ignition temperature and that metals forming peroxides are usually effective. The metal itself when in a state of incipient oxidation is the effective part of the organo-metallic dopes that suppress detonation in an engine, and this metallic oxide is the seat of the action on the combustion process. The most effective metals, with the exception of iron and nickel, are molten and vaporizable at the ignition temperatures.

The colloidally dispersed metals had no effect on the ignition of alcohols but greatly changed the temperature for ignition of aldehydes. The effect

[151] *Compare* Garner and Saunders, *J. Faraday Soc.* 1926, p. 335.

produced was, in general, that of delaying oxidation in a manner similar to that of the organo-metallic compounds which act as knock suppressors.

The oxidation of fuels by adiabatic compression is not markedly affected by the addition of antiknocks in a manner to change the ignition temperature.[80a, b] The addition of toluidine or diethyl sulfide to cyclohexane was found not to affect the temperature of ignition obtained on compression. The results of Tizard, in general, confirm this conclusion. However, the addition of 5 per cent of different antiknocks to 1:17.52 by weight mixtures of hexane-air increases the duration of the combustion period as measured by the duration of pressure rise in adiabatic compression ignition. From a normal period of 0.004 second for the hexane-air mixture, lead tetraethyl raised the time to 0.011 second, toluidine to 0.01 second, methanol to 0.006 second, and diethyl sulfide to 0.005 second.[158]

Layng and Youker studied the effects of different metallic oxides on the rate of oxidation of a gasoline to test the theory that antiknock compounds were effective through the oxide produced by the thermal decomposition and subsequent oxidation of organo-metallic dopes.[4a] Data were obtained by noting pressure changes occurring in a bulb containing the fuel-oxygen mixture and the metallic oxide while maintained at a constant temperature. At 190° C. 2 per cent of ethyl fluid, PbO, Ni_2O_3, Fe_2O_3 retarded and PbO_2 slightly retarded the oxidation. PbO appeared to be the most effective. HgO and MgO appeared not to retard the oxidation. At 210° C. PbO and Fe_2O_3 retarded oxidation while MgO was not effective. At 220° C. the gasoline oxidized quite rapidly, and PbO and 2 to 3 per cent ethyl fluid seemed to stop practically all oxidation. Fe_2O_3 decreased the rate somewhat while MgO was without effect. At this temperature Pb_2O_3, PbO_2 and PbO were practically equal in effect. These results indicate that the action of lead tetraethyl in inhibiting the oxidation of hydrocarbons at elevated temperatures is through the action of the oxides which act as negative catalysts.

Neither Ni_2O_3, Fe_2O_3, ZnO, Al_2O_3, or CeO_2 were as effective in retarding the oxidation of kerosene at 180° C. as were Pb_2O_3, PbO, and PbO_2.

The study of ignition temperatures of fuels with and without antiknocks being present has disclosed a number of anomalies which have not been satisfactorily explained. Despite the low ignition temperature of carbon bisulfide, admixture to the extent of 50 per cent with gasoline has been found to raise the useful compression ratio by 6 per cent.[119, 121, 144] The addition of acetaldehyde to gasoline lowers the ignition temperature but the presence of tetraethyl lead suppresses this lowering effect. The contrary is true of ethyl ether which apparently destroys the efficacy of the antiknock in either suppressing the detonation characteristics of ether-gasoline mixtures or in raising the ignition temperature.

153 Aubert, Dumanois and Pirrot, *Combt. rend.* 186, 1909 9 (1928)

The work of Brown and his coworkers in the study of the propagation of flame and pressure through mixtures of hydrocarbon vapors and air containing decomposed and undecomposed tetraethyl lead has done much to explain some of the contradictions existing in the literature regarding the action of antiknocks on explosive mixtures.[97, 118, 124b, 154] An apparatus which permitted the taking of simultaneous records of pressure and flame propagation was used to obtain a considerable mass of data in regard to the action of tetraethyl lead toward inflamed mixtures of several hydrocarbons with air. The effect of auto-ignition induced by a "hot spot" ahead of the flame front which had been initiated by a spark was studied in relation to the knock suppressing character of the two forms of antiknock used.

Lead tetraethyl, decomposed by dropping the liquid on a red-hot glass surface before mixing with the hydrocarbon-air mixture in the test bomb, is effective in reducing flame velocity, auto-ignition and rate of pressure rise. However, undecomposed lead tetraethyl was ineffective except under such conditions where decomposition would be expected. These results lead to the conclusion that decomposition is required before lead tetraethyl can be effective and confirms the suggestions of Charch, Mack, and Boord[81] and of Egerton and Gates[43] that the decomposition products of antiknocks are the seat of their action. The experiments of Maxwell and Wheeler[89] regarding the effectiveness of the decomposition products of lead tetraethyl are also supported.

Lead tetraethyl starts to decompose in the vapor phase when admixed with air at 230° C.[48] but is not completely decomposed until a red heat has been reached when it inflames with formation of colloidal lead. Lead tetraethyl decomposed up to 230° C. is ineffective in retarding the rate of inflammation,[155] a result which has been confirmed by several workers and has led to controversy.

The effect produced by the addition of lead tetraethyl to the explosive fuel-air mixtures has been shown to be largely governed by the type or rate of combustion following ignition and practically independent of the chemical structure of the fuels. For mixtures giving a maximum rate of pressure rise below a critical value of about 90,000 pounds per square inch per second, 0.1 to 0.2 per cent by volume additions of lead tetraethyl tended to decrease the maximum rate of rise, and greater additions tended to increase the maximum rate. For mixtures giving a maximum rate of pressure rise above this critical rate, 0.1 to 1.0 per cent additions of the anti-knock tended to increase the rate for all the fuels tried. Thus, the effect is dependent upon the normal rate of pressure rise of the fuel, indicating that the effect of lead tetraethyl is due to the presence of decomposition products the rate of formation of which, relative to the rate of release of energy, determines the nature of the effect.

[154] a. Carr and Brown, *Am. Chem. Soc. Meeting Columbus*, 1929; *Ind. Eng. Chem.* 21, 107 (1929); b. Zieganhain, *Oil and Gas J.*, June 12, 1930, p. 34, 140.
[155] Egerton. *Nature* 119, 259 (1927).

Auto-ignition induced by a "hot spot" ahead of the flame front results in a very high rate of energy release as shown by greatly increased rates of rise of pressure and speed of flame. The vapor of lead tetraethyl has relatively little effect on the temperature required at the "hot spot" for auto-ignition or on the flame and pressure propagation resulting from such ignition. Decomposed lead tetraethyl, however, tends to retard auto-ignition of heptane, pentane, and 3-methyl pentane and decreases the rate of flame and pressure propagation following auto-ignition for all fuels. Ordinarily, auto-ignition is preceded by the accumulation of heat during a lag period which raises the temperature to the point of ignition.[73, 158] The decomposed lead tetraethyl apparently lengthens this lag period sufficiently to prevent the setting up of a second flame front which would otherwise result in a greatly increased rate of rise of pressure.

Maxwell and Wheeler [89, 106] found that a 3.8 per cent pentane-air mixture, initially at 15° C. and two atmospheres pressure, exploded with a slight knock, some turbulence of the flame front, and vigorous vibrations in the pressure curve. The addition of 1.18 per cent of lead tetraethyl served to intensify the knock, turbulence, and vibrations. However, decomposed lead tetraethyl eliminated the knock, nearly obliterated the flame front, and caused a very regular rise of pressure. Brown's work confirmed these results and showed further that decomposed lead tetraethyl invariably suppressed the development of the pressure waves into waves of high amplitude or "shock waves," which would ordinarily result from the mutual influence of the pressure waves and a high rate of energy release in the mixture. This effectiveness of the decomposed relative to the undecomposed lead compound may be attributed to the inability of the organometallic compound to decompose and oxidize rapidly enough in the very high speed flame.

Midgley [133] early proposed the idea that knock suppressors were effective by increasing the critical pressure at which "detonation" occurs in the engine cylinder. The effect of knock suppressors in permitting the operation of an engine at a higher compression ratio than possible with an untreated fuel was known and is reflected in the theory. However, the uncertainty that exists today in regard to whether or not it is possible to obtain true detonation in an engine cylinder detracts from the explanation.

Effect on detonation. Egerton and Gates [64, 111] investigated the detonation of mixtures of pentane and acetylene with oxygen and nitrogen mixtures of definite composition, and determined the effect of such factors as composition, nature of diluent gas, pressure, temperature and presence of antiknock compounds. Detonation appeared to occur slightly ahead of the combustion front at ordinary initial temperatures and pressures. Under these conditions the presence of lead tetraethyl or selenium diethyl did not affect the position of detonation. Also, lead tetraethyl was found

[158] Taffanel and LeFloch, *Compt. rend.* 156, 1544 (1913); 157, 469 (1913).

not to affect the position at which detonation occurred in the steel tube at high initial pressures either at low initial temperatures or at 230° C.

Measurements of the velocity and position of detonation of acetylene, hydrogen, and pentane with oxygen, nitrogen, argon, and carbon dioxide mixtures at initial pressures up to 6 atmospheres were also made.[157] The presence of antiknock compounds was found not to affect the position of detonation. Lead tetramethyl delayed the rate of combustion of pentane, however.[158, 43]

These results cast doubts on the theory that the knock is caused by true detonation taking place during the operation of an engine. However, the photographic records of the explosions of gaseous hexane-air mixtures initially at 80° C. obtained by Duchene failed to show the propagation of a detonation wave when 5 per cent of lead tetraethyl was present in the hexane, although without the antiknock such detonation appeared in the record.[159] Also, additions of selenium diethyl, tin tetramethyl, or lead tetramethyl to air-hydrocarbon mixtures have been found to decrease flame speed in horizontal, closed, glass tubes.[160] However, in this latter case the results are confused because of the effect of turbulence in the gas mixture during combustion.

Effect on oxidation reactions. From a study of the oxidation of the isomeric octanes, Pope, Dykstra, and Edgar [42] showed that the reaction proceeded by a chain mechanism and that the decomposition of the peroxide first formed between a hydrocarbon and an oxygen molecule resulted in the release of an aldehyde in a high state of activation which underwent further oxidation through a continuation of the chain. The proposed reactions for the oxidation of n-octane are as follows:

$$CH_3(CH_2)_6CH_3 + O_2 \quad = CH_3(CH_2)_6CHO + H_2O \tag{1}$$
$$CH_3(CH_2)_6CHO + O_2 \quad = CH_3(CH_2)_5CHO + H_2O + CO \tag{2}$$
$$CH_3(CH_2)_5CHO + 1.5O_2 = CH_3(CH_2)_5CHO + H_2O + CO_2 \tag{3}$$
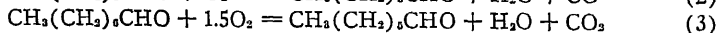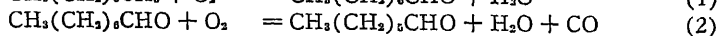
The most striking effect of lead tetraethyl in the reaction with n-octane is on the reaction producing carbon monoxide, reaction 2. Although oxidation starts at about the same temperature as without the antiknock, the consumption of oxygen rises with increases of temperature more slowly than can be accounted for by the suppression of carbon monoxide formation particularly at low and intermediate temperatures. This indicates that the primary oxidation of the hydrocarbon (reaction 1) to aldehyde is retarded and that complete oxidation requires a higher temperature than when lead tetraethyl is absent. The disturbance which normally occurred in the reaction zone at a low temperature, takes place at a more elevated temperature when lead tetraethyl is present.

Practically the entire effect of the antiknock is on the reaction pro-

[157] Egerton and Gates, *Proc. Roy. Soc.* 116A, 516-29 (1927).
[158] Egerton, *Nature* 121, 876 (1928); 122, 20-6 (1928).
[159] Duchene, *Compt. rend.* 187, 200-1 (1928).
[160] Nagai, *J. Soc. Chem. Ind.* (*Japan*) 33, Suppl. binding 117-20, 296-9 (1930); *Chem. Abs.* 24,

ducing carbon monoxide when n-heptaldehyde is oxidized. The carbon dioxide reaction is not affected. The reduction in carbon monoxide formation is equal mol for mol to the decrease in oxygen consumption. The lead tetraethyl probably acts by absorbing the energy of the active molecules in the reaction chain which gives rise to carbon monoxide (reaction 2).

An increase in the concentration of lead tetraethyl from 0.31 per cent by volume to 1.0 per cent does not produce a corresponding effect on the phenomena attending oxidation.[180] The effect is more pronounced at the lower temperatures and tends to decrease as the temperature is raised. The probability that the more readily oxidized hydrocarbons undergo reaction during the compression stroke of the engine and before spark ignition and that the extent of this oxidation determines the tendency to detonate has been pointed out. Also, it has been shown that the reaction velocity during knocking operation of an engine is considerably higher than during normal operation.[148] The fact that lead tetraethyl reduces the low temperature oxidation is indicative of its action in reducing knock. The fact that a concentration of one molecule of lead tetraethyl in 200,000 molecules of kerosene is capable of suppressing knock makes it appear that an action similar to that of catalysis is in effect. Also, the antiknocks do not appear to affect equilibrium but simply alter the rate of approach to equilibrium, i.e., slow down combustion. The essential difference between the operation of an antiknock dope and a catalyst is that the dope is changed in the process, whereas true catalysts remain unaltered.

The presence of organic peroxides has been shown to increase the knocking tendency of a fuel and to lower the ignition temperature. Peroxide formation has, hence, been associated with knocking. On the other hand, no active oxygen or peroxides have been shown to occur during the combustion of fuels when an active antiknock compound is present, and the conclusion that has been reached is that antiknocks decrease knock by preventing peroxidation. The proof of this has been found to be rather difficult. Evidences of autoxidation through peroxide formation and the effect of dopes such as lead tetraethyl on autoxidation have accumulated. Such results cannot be applied directly to knocking. This is shown in the case of deca- and tetrahydronaphthalene which form peroxides and undergo autoxidation very readily and which are, nevertheless, relatively non-knocking motor fuels.[59]

Ionization. The electric current between two platinum plates held in a flame increases as the potential difference between the plates is increased. The curve obtained by plotting current against potential difference resembles that obtained with an ionized gas and may be represented by the equation: [101]

$$i^2 = (\text{constant})(V)$$

[101] Crowther, "Ions, Electrons, and Ionizing Radiations," p. 139 (1929), Longmans, Green and Co.

where i is the measure of current and V of the potential difference. The fact that flames are ionized has led to a study of the effect of knock suppressors on the ionization of burning mixtures of fuel and air with a view to explaining the action of knock suppression, and of the effect of ionizing influences on the combustion process.

It is generally conceded, however, that ionization does not play a primary rôle in flame propagation and that it is manifest rather as a result than a cause. The experimental work has not removed the doubt concerning that increased ionization may as well be an accompanying phenomenon to knocking as a cause of it.[61, 102]

The oxidation of methane with an equivalent of oxygen by radon radiation both with and without 0.001, 0.01, and 0.046 mol fraction of diethyl selenide, an antiknock, has shown that the presence of the antiknock does not retard but rather accelerates the reaction.[103] That the acceleration may be due to the absorption of the alpha radiation by the metallic compound, which then acts as a medium for the activation of the molecules of oxygen and fuel, has been proposed to explain the effect. Lind also makes the suggestion that the absorption of other forms of radiant energy, such as infra red radiation, by the antiknock may be the function of the antiknock during combustion processes. Such absorption would lead to the multiple-ignition theory mechanism of a homogeneous pre-combustion prior to the passage of a flame front through that part of the mixture which burns last.[104]

Ionization is one of the later steps of combustion and is not the essential first step. The presence of ions formed by β rays from radium bromide makes no difference in the ignition temperatures of fuels.[17, 18] The primary step in combustion is the combination of oxygen molecules with fuel molecules, but as the temperature at which this combination occurs increases and the energy level of the molecules becomes greater, ionization occurs as a late stage of the process.[141] The conclusion has been that ionization in gaseous explosions is mainly a thermal process and that the action of knock inducers and suppressors on combustion phenomena cannot be adequately explained on the basis of ionization effects.

It has been proposed,[134] however, that electrons shot from the advancing flame front into the unburned portion of the cylinder charge caused ionization and consequent activation of the fuel and oxygen molecules and resulted in a greatly accelerated rate of flame movement through the combustible mixture. This proposed mechanism has been shown to be out of accord with experimental facts.[105]

The release of large amounts of energy during the early portion of the burning period in an engine cylinder, manifested as light extending well into the ultra-violet region of the spectrum, has been found to take

[102] a. Garner and Saunders, *Trans. Faraday Soc.* 22, 281 (1926); b. Finch, *Proc. Roy. Soc.* 111A, 257 (1926).
[103] Lind and Bardwell, *Ind. Eng. Chem.* 19, 231-3 (1927).
[104] Lind, *J. Chem. Soc.* 125, 1867 (1924).

place during knocking operation.[81, 120a] The effect of knock suppressors has been shown to be a restoration of the emitted spectrum to normal proportions; but is of little significance since the emission characteristics appear to be an effect of knocking operation rather than the cause of it. Similar effects of suppressed luminosity have been found in the explosions of fuel-air mixtures in long glass tubes. Lead tetraethyl has been observed to prevent the return of luminosity to the portion of the charge already modified by the explosion, a phenomena known to occur in long tubes when explosive mixtures are ignited by spark from one end. The importance of this "after burning" effect on knocking has been open to question.

THEORIES OF ANTIKNOCK ACTION

In a broad way, the theories that have been advanced to explain the mechanism by which antiknocks operate may be divided into those which assign only a passive rôle to the antiknock and those which assign an active rôle.

Film theory. The theory that the metal parts of the cylinder walls act as positive catalysts in increasing the flame speed to detonation velocity and that antiknocks act as poisons to destroy the catalytic activity by depositing on the walls is open to the objection that the knock disappears immediately that a dope is added and reappears with no appreciable lag when the addition is discontinued.[106] Other factors to be considered are that organic amines, iodine, selenium, lead, and other antiknock dopes are known to act as poisons toward certain catalysts whereas mercury and sulfur, potent catalyst poisons, are knock inducers. Also, the action of lead tetraethyl in retarding the liquid phase oxidation of benzaldehyde is not explainable on the basis of a poisoning action exerted on the glass walls, since the reaction has been found to proceed equally as well in a lead as in a glass vessel.

A somewhat similar theory [107] postulates the formation of colloidal lead by the decomposition of lead tetraethyl, which deposits on sharp points, edges, and projections in the cylinder which would otherwise aid reaction to an extent that a detonation wave would result. The theory fails to explain the action of organic amines, of di- and tetravalent selenium, of the colloidal metal sols, and fails to account for the immediate recurrence of knocking when the antiknock dope is discontinued in the gasoline feed. However, tubes coated with lead oxide have been found to reduce the oxidation of hexane more than lead tetraethyl vapors.[108] On the basis of this finding the hypothesis was advanced that oxidation occurs to some extent prior to compression and at the first contact of the gaseous mixture with the hot walls, and that in the presence of the lead

[106] a. Turner, *Edinburgh Phil. J.* 11, 99 (1824); b. Schlesinger, *J. Soc. Auto. Eng.* 16, 441 (1925).
[107] Jolibois and Normand, *Compt. rend.* 179, 27 (1924).
[108] A.P.I. Research Program, *J. Inst. Pet. Tech.* Apr. 1930, p. 336-8.

the hexane molecule remained less activated after the first oxidation step.[169]

The effect of ethylene, acetylene, methane and nitrogen peroxide in inhibiting the phosphorescent oxidation of carbon disulfide has been explained by Dixon as due to the formation of a film about the "nodes of reaction."[170] Davy[171] showed that hydrogen sulfide, hydrogen chloride, methane, and acetylene exercised an inhibiting action in the explosion of gaseous mixtures. Other workers have likewise observed that small amounts of certain gases restrained the burning of combustible mixtures.[172] In explaining the action of antiknocks in the light of his nuclear-drop theory of knocking, Callendar[14] assumed that a condensation of the colloidal cloud of metal particles, formed by decomposition of the organic compound, occurred on the surface of the liquid drops. In the case of the organic amines, Callendar's study of the antiknock value, critical temperature, boiling points, and ignition points showed a close relation to exist between these properties. The effect is attributed to the concentration of the amine in the nuclear drop. The discord existing in regard to the effects produced by colloidal metals on knocking, the lack of evidence to show how the concentration of the dopes at the nuclei surface is effective, and the fact that Callendar considered saturated vapors in proposing his theory—all militate against this theory. The action of the droplets in promoting knocking was through the formation and accumulation of organic peroxides which promoted the autoxidation of a portion of the charge and thus induced a very rapid combustion. The antiknocks accumulating in the droplets were effective as inhibitors to this process of autoxidation.

Radiation screen theory. Midgley[188] adopted Perrin's theory, that radiations from the initial flame activate and accelerate reaction by splitting the hydrocarbons into a more reactive condition, in explaining knocking and assumed that antiknocks acted as screens for absorbing the radiation and controlling the velocity of flame movement. Experimental proof in support of this theory has not been obtained and its merit will be difficult to demonstrate. The theory is not adequate, however, to explain the action of knock inducers.

Buffer theory. That antiknocks are effective as buffers, because of inertia of the molecule, to absorb the energy of agents active in the propagation of reaction has been proposed by a number of scientists. Such agents comprise the active molecules of chain reactions, which will be discussed separately, electrons, or ions.[184, 178] Part of the energy released

[169] Zeikowsky, Holroyd, and Sokoloff, *Phys. Rev.* 33, 264 (1929); *Chem. Abstracts* 24, 4620 (1930).
[170] Dixon, *Rec. trav. chim.* (4), 44, 305 (1925).
[171] Davy, *Phil. Trans. Roy. Soc.* 1817, 45.
[172] a. Frankland, *J. Chem. Soc.* 16, 401 (1863); b. Turpin, *Rept. Brit. Assn. Adv. Sci.* (1890); c. Tanatar, *Z. phys. Chem.* 35, 340 (1900); d. Bucher, *Z. Ver dcut. Ing.* 55, 1110 (1911); e. Jorissen, *Rec. trav. chim.* 39 (4), 715 (1920); 43 (4), 80, 591 (1924); 44 (4), 132, 810, 815, 1039 (1925); 45 (4), 163, 224 (1926).
[173] Muraour, *Chimie et industrie* 14, 851 (1925) (191T).

by reactions in the flame front has been postulated to be used in the projection of electrons into the unburned charge in front of the flame where they cause ionization of the combustible. This ionization would serve to activate the reacting molecules so that reaction velocity would be increased and detonation induced. Increased temperature and pressure promote knocking due to the effect in increasing the liberation of electrons.

Tetraethyl lead is supposed to function by reducing the ionization of the unburned mixture directly ahead of the advancing flame front, and thus preventing the undue acceleration of combustion which leads to knocking. This reduction in ionization was by the suggested absorption of ions by the lead atoms and their discharge through recombination.

The theory implies that knock inducers act by increasing **ionization** an effect not observed. The experiments of Wendt and Grimm furthermore did not show the effect of electric and magnetic fields upon the velocity of propagation of detonation waves found by Lind.[174] In repeating the experiments of Wendt and Grimm under carefully controlled conditions, Clark, Brugmann and Thee were unable to confirm either the theory or the experimental results. Their results indicate that the theory of electron wave fronts and the absorption of electrons by antiknocks is inadequate to explain the effects produced during engine operation. The work of other investigators has led to similar conclusions.[61, 162a] Garner and Saunders provided the only positive evidence that lead tetraethyl had any effect on ionization but under conditions such that it would have had no effect on the velocity of flame propagation in an engine cylinder.

That one molecule of lead tetraethyl in 200,000 of gasoline should be as effective as a 25 per cent benzene addition in suppressing knock is also difficult to account for on the basis of simple absorption of energy from electrons projected from the burning zone.

Partial combustion theory. It has been suggested [61] that lead tetraethyl is active by means of inducing a pre-combustion in the vapor-air mixture present in the engine cylinder. The theory postulates an immediate oxidation of the active lead particles formed by the decomposition of the organic compound which raises their temperature above that of the unburned, surrounding combustible mixture. These particles act as centers of oxidation during some stage of the engine cycle and thus induce a homogeneous combustion of the gas ahead of the flame front. The antiknock thus functions as an auxiliary ignition system to start oxidation ahead of the actual flame. Ordinarily, the gaseous mixture ahead of the flame would not be ignited until the flame had passed or until it had been ignited ahead of the flame by rise in temperature and pressure caused by the initial burning of a portion of the mixture. This more regular and more uniform combustion supposedly suppressed the detonation or knock which would ordinarily occur.

[174] Lind and Bardwell, *Brennstoff Chem.* **7**, 286 (1926).

The findings of Olin, Read and Goos that colloidal metals do not affect the knocking properties of a fuel do not necessarily invalidate this theory since the metal particles formed in the gaseous mixture may be in a much higher state of activity. It should be noted, however, that the colloidal metals that have been used in knock testing work have been sufficiently active to be pyrophoric. However, the experimental evidence has shown that lead tetraethyl has no influence on the length of the preliminary run before detonation or on the rate of inflammation of gasoline-air mixtures at normal temperatures and pressures in closed cells.[112, 155, 175] It is prob-able that did the particles of the lead cloud induce preliminary combustion at a low temperature that some effect would be noted on the length of preliminary run.

The multiple-ignition theory is also not in accord with the fact that increase of initial temperature, such as would be produced by an action as described, tends to increase the tendency for knocking. If such homogeneous pre-ignition did occur, the rate of temperature rise throughout the engine cylinder would be favored rather than hindered. Also, since lead tetraethyl vapor in air does not start to decompose until a temperature of 230° to 250° C. has been reached and is not fully decomposed until red heat is attained, it is not apparent that such partial combustion could occur during the compression stroke of the engine and prior to spark ignition.

The theory in common with a number of the others does not explain the antiknock action of the organic amines nor does it explain the action of knock inducers. It is not clear why triethylchlorolead and diethyldichlorolead should be, respectively, 75 per cent and 50 per cent as effective as tetraethyl lead.

Antioxidant theory. Since by far the greater part of the experimental evidence has shown that antiknocks act by suppressing combustion, reducing flame speeds, raising the temperature for ignition of fuels, and reducing the rate of autoxidation reactions, they may reasonably be looked on as antioxidants. Also, among the several possible mechanisms that have been proposed for the gas phase oxidation of motor fuels, the one involving a chain of reactions best meets the requirements.[176]

The idea that the processes, which occur during the combustion of a fuel in an engine cylinder, take place by a chain reaction mechanism comparable to that associated with the liquid phase autoxidation of benzaldehyde, has led to the proposal that knock suppressors act by destroying the chains and reducing the rate at which the flame front accelerates. It is known that surfaces or solid bodies suppress chain reactions, in fact one of the criteria for a chain reaction in gaseous combustion processes is the decrease in rate of reaction caused by the increase in surface exposed to the gases. However, the mode by which the chains are broken or

[175] a. Maxwell, *Fuel Sci. Pract.* 6, No. 3 (1927); b. Dixon, *Trans. Faraday Soc.* Oct. 1926, p. 372.
[176] Compare Dumanois, *Compt. rend.* 186, 292-3 (1928).

stopped is not so clearly defined.[177]   In the case of such knock suppressors as lead tetraethyl, or iron pentacarbonyl the particles of metal, released by the decomposition of the organic molecule at the temperature of the gases in the engine cylinder, may act as do solid surfaces in breaking the chains.   It is also possible that the compounds act as negative "catalysts," as Bäckström [80] has suggested, by becoming oxidized by the active intermediate products of the chains.   Or the antioxygenic action theory of Moureu and Dufraisse, by which the antiknock is regenerated after reaction with an active intermediate product may hold.   In combustion processes the propagation of reaction chains by means of "hot" molecules as proposed by Bodenstein [35] is a more acceptable mechanism than the material chain as proposed by Nernst for reactions involving the production of chlorine atoms.   Since this is so, the mechanism by which the knock suppressors can be effective is limited to either absorption of the energy of the "hot" intermediate molecules of a chain or to interaction with them to prevent a contamination of the chain by further reaction of fuel and oxygen as was suspected by Davy in 1817.

The oxidation of pure benzaldehyde in oxygen at 25° C. is accompanied by an induction period during which absorption of oxygen is slow. After the induction period the oxygen consumption increases rapidly and finally attains a maximum rate.   The presence of benzoyl peroxide reduces the length of induction,[12] and results in a higher final velocity of oxidation. On the other hand, phenol, benzyl alcohol, lead tetraethyl, and metals dispersed in benzene increase the length of the induction period and act as inhibitors.   The effect of the inhibitors probably occurs as the result of action during the induction period through hindering the normal peroxide formation.   The addition of benzoyl peroxide along with metal sols greatly reduces their influence on the reaction rate.   The addition of ferrous chloride accelerates the reaction in aqueous solution, and the addition of slightly more than an equivalent quantity of ferrous chloride may completely overcome the inhibiting action of an iron sol.

That antiknocks are effective in retarding liquid phase oxidations that are propagated by chain reactions is shown by the fact that the rate of oxidation of 5 cc. of benzaldehyde was reduced from 1.5 cc. of oxygen absorbed per minute to 0.005 cc. of oxygen absorbed per minute by the addition of one drop of lead tetraethyl to 5 cc. of aldehyde.[178]   The effect of oxidation inhibitors, as phenol or aniline on gaseous oxidation of fuels is similar to their effect on liquid phase oxidation of benzaldehyde.[17]

In considering the effect of knock suppressors on chain reactions, the significant correlation found to exist between the action of lead tetraethyl in reducing knock and in suppressing certain oxidation phenomena in the oxidation of n-octane, should be pointed out.[42]   Engine tests have shown that the isomeric octanes may be arranged in decreasing tendency to knock

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[177] Bodenstein, *Chem. Rev.* **7**, 220 (1930).
[178] Taylor, *Nature* **119**, 746 (1926); *Ind. Eng. Chem. News Ed.* February 1924; *Chem. Met.* **30**, 148 (1924).

in the following order: n-octane, 3-methyl heptane, 3-ethyl hexane, 2-methyl-3-ethyl pentane, 2,5-dimethyl hexane, and 2,2,4-trimethyl pentane, which is the same order of their tendency to oxidize when tested in a flow system. In the oxidation of these five isomers and n-octane one of the chief reactions is the oxidation of an aldehyde to carbon monoxide, water, and an aldehyde with one less carbon atom, by a chain reaction mechanism. In the case of the isomers this reaction starts at the end of the longest carbon chain of the hydrocarbon molecule and proceeds without interruption to the branch. When reaction reaches the branch in the carbon chain, oxidation slows down. Thus, the more-branched hydrocarbons, which show the least tendency to detonate, oxidize with the lowest rate. The addition of lead tetraethyl vapors sharply reduces the chain reaction normally giving rise to carbon monoxide and aldehyde, and in this way gives an effect similar to that obtained by making the hydrocarbon more branched. Similarly, this knock suppressor reduces knock in a manner paralleling that caused by branching the molecule.

Despite the large amount of work that has been done by Bone and his co-workers and by the antagonists of the hydroxylation theory of hydrocarbon oxidation, it is not clear whether the first step in the process represents the formation of an aldehyde by oxidation with a molecule of oxygen or the formation of an hydroxylated hydrocarbon by the addition of an oxygen atom. However, alcohols have not been detected in the products of ordinary combustions, aldehydes have been found in large quantities, and the presence of peroxides proved. The evidence in favor of a peroxide method of oxidation, propagated through a chain mechanism, is quite strong and has furnished a basis for explaining the mechanism of anti-knock action.[170]

The mechanism of antioxygenic action as proposed by Taylor[51a] involves the direct inactivation of active oxygen molecules or active molecules of the autoxidizable substance by the formation of a temporary combination of the antioxidant molecule with the active fuel or oxygen molecule followed by dissociation and the liberation of inactive molecules. This theory has been attacked by Moureu and Dufraisse[47] on the ground that the great variety of antioxidants and of autoxidizable substances makes the postulates improbable. The only constant factor is the presence of oxygen. Also, in the case of the autoxidation of acrolein, the inactivation of acrolein molecules by the antioxygen, hydroquinone, is insufficient to account for the observed antioxygenic action.[180] Moureu believes in a mechanism as follows:

$$A + O_2 = A[O_2]$$
$$A[O_2] + B = A[O] + B[O]$$
$$A[O] + B[O] = A + B + O_2$$
$$\text{or } A[O_2] + A = 2A[O] = 2AO \text{ (stable oxygenated product)}$$
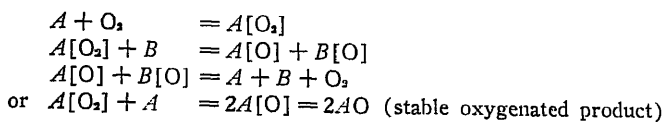
[170] a. Bone, *Nature* 122, 203-4 (1928); b. Egerton, *ibid.* 204.
[180] Moureu, Dufraisse, and Badoche, *Bull. soc. chim.* (4), 35, 1564 (1924).

where A is the oxidizable substance and B is the antioxidant. Whether the peroxide acts as a negative or positive catalyst depends on the concentration of oxygen (pressure) and the stability of $B[O]$. Since only organo-metallic compounds of metals that form stable oxides and are capable of existing in more than one degree of oxidation are active as knock suppressors it may be inferred that some sort of intermediate formation does take place between the metal atom and the organic peroxide. Purely organic antiknocks as aniline are only effective in much larger quantities than the metallic compounds since they are destroyed by oxidation during the combustion. Since colloidally dispersed metal oxides are ineffective in retarding hexane oxidation whereas the same metals are, it may again be inferred that mere interruption of a reaction chain by absorption of energy is insufficient and that formation of intermediates is essential to actual retardation.[181]

A close relation exists between the antiknock action of metals and the character of their oxides. The regeneration of the metallic peroxide by interaction with a peroxidic molecule of combustible after the metal peroxide had been reduced by the action of a molecule of unoxidized fuel is possible. That such a mechanism requires the metal or peroxide to be in a molecularly divided state accounts partly for the contradictory results obtained with "artificially" generated metal fogs. A certain state of equilibrium appears to exist between oxidized products of the organo-metallic antiknocks.[182] In the case of potassium, the oxides K_2O_3 and K_2O_4 have been shown to exist in a state of equilibrium in favor of the higher oxide at 400° C. This higher oxide may be reduced by an active fuel molecule and the lower oxidized by impact with an oxygen molecule. The breaking of reaction chains by this successive reduction and oxidation process is also indicated by the small amount of antiknock necessary to produce pronounced effects in the engine. Ether inhibits the action of lead tetraethyl as an antiknock by forming a fairly stable oxidation product with it. Nickel carbonyl does not form a similar compound and is not counteracted by ether in its action.

That the presence of aldehydes and organic peroxides in hydrocarbon-air mixtures favors ignition and promotes knocking seems to show that antiknocks are effective in the early stages of the combustion process by suppressing the initial formation of peroxides and retarding the formation of aldehydes which have a large tendency to form peroxides. This mechanism, involving as it does the breaking of reaction chains, explains the relatively enormous effects produced on ignition and knocking by very small amounts of knock suppressor. Such an action would necessarily have to occur largely during the induction and compression strokes of the engine, and although it would possibly preclude the action of metal clouds formed by thermal dissociation of the organo-metallic compounds, has,

[181] Berl and Winnacker, *Z. physik. Chem.* 145A, 161-76 (1929); *Chaleur & Ind.* 11, 23-30 (1930).
[182] Egerton, *Proc. Roy. Inst. Gt. Brit.* 1928, 15 pp.; *Nature* 122, 20-6 (1928).

nevertheless, been subscribed to.[62]   The studies of the effect which knock inhibitors have in decreasing emission of light of great intensity during the early part of the explosion in an engine supports the view of an effect during the early part of the cycle.

A similar explanation may be advanced for the case of the purely organic compounds which inhibit knocking.   Such compounds have been shown to form peroxides [188] which are probably of sufficient thermal stability to produce effects comparable to the metallic compounds.[184]   However, relatively little is known in regard to these substances as far as their behavior at temperatures existing under combustion conditions is concerned.

[183] Bach, *Compt. rend.* 126, 951 (1897).
[184] Staudinger, *Ber.* 58, 1075 (1925).

Chapter XII

The Oxidation of Benzene and Its Derivatives

The oxidation of benzene and its derivatives has been the subject of careful investigation ever since the structural formula for an aromatic complex was first suggested by Kekulé. The results of these many and varied experiments have served to show that in the case of all such compounds the phenomena of oxidation are very complex. Even benzene itself under the influence of oxidizing agents reacts under different conditions to give a great variety of different products.

In the case of benzene the primary effect of heating, with or without the presence of oxygen or of catalysts, is to dissociate a single hydrogen atom. This may be accompanied by the condensation of the residues to form diphenyl. The homologs of benzene behave in an analogous manner under similar conditions and the corresponding derivatives of diphenyl are produced.

If oxygen is present the same result may be obtained or various oxidation products of benzene may be formed. In the latter case the primary action of oxidizing agents under certain conditions results in the formation of phenol. Further oxidation affects other hydrogen atoms (viz., in the ortho and para positions respectively) with the formation of catechol and quinol. These substances readily undergo further oxidation and are transformed into the corresponding quinones. In the case of all of these reactions, conditions may be so regulated as to favor the formation of any one or more of the above mentioned oxidation products. On the other hand, the conditions may be such as to give rise to different condensation products derived from them. For example, by distilling phenol with plumbous oxide, diphenylene oxide may be produced.[1]

Further oxidation of the quinones is accompanied by an opening of the ring structure. The products in this case are again observed to differ very considerably, depending upon slight changes in operating conditions. The resulting substances belong to the general class of aliphatic compounds conspicuous among which are to be found adipic acid $HOOC-(CH_2)_4-COOH$; butadiene, $CH_2=CH-CH=CH_2$; maleic (and fumaric) acid, $HOOC-CH=CH-COOH$; and oxalic acid, $HOOC-COOH$. Derivatives of the quinones open up in an analogous manner to give corresponding derivatives of the above types. In the case of the derivatives of

[1] Täuber and Halberstadt, *Ber.* **25**, 2745 (1892); *also* Knicht and Unzeitig, *Ann.* **209**, 34 (1881).

benzene still another mode of oxidation has been observed, i.e., side chains may be attacked by the oxidizing agent while the nucleus itself remains intact. In such cases, the products consist respectively of benzaldehyde or benzoic acid or various derivatives of these substances. This particular type of oxidation appears to be attended by fewer complications and to be controlled more readily than either of the other two which involve respectively the oxidation of the hydrogen atoms of the ring or a break-down of the entire ring structure. There are, therefore, a greater number of examples of side-chain oxidations to be found in the literature. Particularly, in the case of oxidations with air or oxygen in the vapor phase, operations of this character have proved successful and have been carried through with exceptionally good results.

In order to simplify as far as possible the very complex data dealing with the oxidation of benzene and its various derivatives, the phenomena will be considered in the following order: (a) oxidations involving the formation of diphenyl and its derivatives; (b) oxidations involving the formation of phenols and quinones; (c) oxidations accompanied by a break-down in the ring structure; and (d) oxidations which primarily involve the side chains present in the homologs of benzene and their respective phenolic or other derivatives. In the case of each of these principal types of oxidation, it has been deemed advisable to review briefly the main facts which have been established as the result of investigations which have been carried out in the liquid phase. In this way, it is hoped that the important chemical relationships of the substances whose transformations are to be considered may be kept well in mind.

Diphenyl Formation

Diphenyl may be produced from benzene and its derivatives in a number of ways, for instance by passing the vapor of boiling benzene suspended in a stream of carbon dioxide through a red hot iron tube filled with pumice stone. The reaction gases containing unacted-upon benzene are recirculated and the product is then condensed and distilled from a water bath. The residue remaining in the flask after distillation consists of diphenyl which may then be purified by further distillation with steam.[2] The phenomenon was first observed by Berthelot[3] in 1866 and has since been modified in a great variety of ways. For example, diphenyl may also be obtained by passing the vapors of benzene over heated lead oxide[4] or glowing antimony trisulfide;[5] or by passing benzene vapors mixed with air and steam through a clay tube heated at 500° C., preferably in the presence of vanadium compounds.[6] The latter process is covered by a

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[2] Hübner, *Ann.* **209**, 339 (1881); *compare also* Döbner, *Ann.* **172**, 110 (1874); Schultz, *Ann.* **174**, 203 (1874); Hübner and Lüddens, *Ber.* **8**, 870 (1875); apparatus for this process is described by LaCoste and Sorger, *Ann.* **230**, 5 (1885).

[3] *Ann. chim. phys.* (4) **9**, 454 (1866); *Ann.* **142**, 252 (1867).

[4] Behr and Van Dorp, *Ber.* **6**, 754 (1873).

[5] Mertz and Weith, *Ber.* **4**, 394 (1871). For a large number of other methods *consult Beilstein* **V**, 577 (1922).

[6] Walter, Ger. Pat. 168,291 (1904); *also* French Pat. 360,785 (1905); Brit. Pat. 21,941 (1905).

patent which is very general in its scope and which also gives examples for the manufacture of benzaldehyde from toluene, phenylene-oxide from phenol, β-naphthol from naphthalene, etc. In connection with the manufacture of diphenyl, the claim is made that while it is already known that this substance is formed by passing the vapors of benzene through a glowing tube, the rate of flow must under these conditions be very slow. According to the present process, on the other hand, the rate of flow may be greatly accelerated. Means are provided for maintaining constant temperatures in the reaction chamber, which may consist of a bundle of tubes heated externally. The following substances are also claimed as catalysts: platinum, iridium, palladium, silver, uranium, vanadium, cobalt, nickel, cerium, thorium, copper, manganese, titanium, tungsten; also, lead oxide by itself or mixed with calcium oxide; chromium oxide or mixed with aluminium oxide or with calcium oxide to which potash may, under certain circumstances, be added. Oxides of molybdenum and thallium may also be employed.

Another patent refers specifically to the manufacture of diphenyl from benzene in a novel and highly advantageous manner.[7] The invention is based upon the discovery that the amount of diphenyl obtained from benzene can be very materially increased by subjecting the vaporized benzene to a temperature of 700° C. and a pressure of about 60 pounds per square inch in admixture with a diluent gas or vapor (23 parts volume of water vapor). The production of diphenyl can be further promoted by treating the benzene in the presence of appropriate substances which provide cracking surfaces, such as, for example, pumice.

The product of the reaction after liquefaction separates into two layers, one an aqueous layer and the other a hydrocarbon layer containing diphenyl and the unchanged benzene. The latter mixture is separated by distilling off the benzene from the diphenyl and returning it to the process. The diphenyl which is obtained in this way as the result of a single distillation is in a relatively pure state.

Diphenyl may be formed on a large scale by passing benzene vapors through a metal coil immersed in a lead bath maintained at a temperature of 600° to 650° C., which is below the temperature required for the reaction, and then through a similar arrangement in which the temperature of the lead is 750° to 800° C. The first coil serves to preheat the vapors which are rapidly brought up to reaction temperature in the second coil. A water-cooled condenser is used to collect the product.[8] The disclosures set forth in this patent indicate that the use of special catalysts or diluents is not necessary for the successful operation of a diphenyl process and they also indicate that a temperature of at least 750° C. is required for commercial scale reaction rates to be obtained. Unless the splitting off of hydrogen atoms from benzene is aided by the presence of oxidizing con-

[7] U. S. Pat. 1,322,983 (1919) Weiss and Downs assrs. to the Barrett Co.
[8] Brit. Pat. 312,902 (1929) Scott assr. to Federal Phosphorus Co.

ditions, it is not very probable that diphenyl formation occurs to any great extent in the oxidation of benzene which is usually carried out at the lower temperature range of 400° to 500° C.

By applying high pressures of hydrogen to diphenyl at temperatures of about 450° to 480° C., Orloff [9] was able to reverse the reaction and obtain benzene from diphenyl thereby establishing the reversibility of the reaction. At low pressures of hydrogen, however, equilibrium favors diphenyl formation at temperatures above 500° to 550° C.[10]

The adaptability of diphenyl for use as a boiler fluid or for a heat exchange medium has been well demonstrated by the relatively large amount of research done with it. Methods used at present for the manufacture of this substance from benzene have been so successful that the industrial price has fallen to a point where it may be considered for large scale use.[11]

Phenol Formation

Attempts at the direct oxidation of benzene to phenol by the use of molecular oxygen without catalysts have led to the formation of complete oxidation products. This is due largely to two factors. In the first place, the temperature required for the action of molecular oxygen on benzene is so high that the benzene ring becomes unstable and is subject to complete break-down. As soon as the ring ruptures, the residue assumes the nature of an aliphatic compound and as such oxidizes and decomposes at a very rapid rate. Since the aliphatic hydrocarbons are much less stable to both oxidation and decomposition than are the aromatics, a ring once broken is subject to rapid destruction and no "useful" products result. In the second place, there are two available atoms of oxygen per molecule and as benzene requires the introduction of but one atom to form phenol, the second atom of oxygen, in a highly active condition, may be left free in the vicinity of the supposedly newly formed phenol molecule. If such a condition exists, further oxidation is inevitable. To eliminate as far as possible these two adverse factors it has been necessary to seek catalysts that would lower the temperature required for the oxidation and that would release atomic oxygen for the oxidation. An alternative method of overcoming the second objection might be the use of a reactant that could consume the unwanted atom of oxygen. A supply of extra hydrogen as would be had in hydrogenated benzene is an example.

The oxidation of benzene to phenol by means of oxygen or air has been carried out successfully in the liquid phase by a number of investigators but as far as can be learned from a review of the general literature, the percentage yields have, in most cases, been exceedingly low. It was observed, for example, as early as 1878, that aluminum chloride causes

[9] Orloff, *Ber.* **60**, 1950 (1927).
[10] Zanetti and Egloff, *J. Ind. Eng. Chem.* **9**, 350 (1917); Pyl, *Ber.* **60** (B), 1133 (1927).
[11] For physical properties of diphenyl *see* (a) Chipman and Peltier, *Ind. Eng. Chem.* **21**, 1106 (1929); (b) "Physical Properties of Diphenyl," Birmingham, Ala., Swann Chem. Co., 1930.

the direct fixation of atmospheric oxygen by aromatic compounds. Thus, when air is passed through boiling benzene in the presence of this catalyst, phenol is formed and when the same process is applied to toluene, benzoic acid is obtained.[12] Other catalysts, such as sodium hydroxide[13] and palladium hydride[14] in aqueous solution, and even sunlight[15] have been observed to produce the same effect. In the latter case the phenomenon has been interpreted as due to the oxidizing actions of hydrogen peroxide, which may be assumed to have been formed under the conditions of the experiment. Such an explanation is tenable because of the fact that hydrogen peroxide has been observed to oxidize not only benzene to phenol but naphthalene to naphthol and anthracene to anthraquinone.[16] The most successful application of this general method was affected by Cross, Bevan and Heiberg,[17] who were able to obtain 15 per cent of the theoretical yield of phenol along with 3.5 grams of catechol from 10 grams of benzene by the action of hydrogen peroxide in the presence of ferrous sulfate as a catalyst, at a temperature of 45° C. Large yields of tarry polymerization and condensation products were obtained in practically all cases.

The presence of oxides of certain metals of the fifth and sixth groups of the periodic system, such as vanadium, molybdenum, tungsten, or uranium, in a hot aerated benzene-caustic emulsion makes possible the formation of the monohydroxylated derivative of benzene to the exclusion of the undesirable polyhydroxylated derivatives and tarry condensation products.[18] The operating conditions are stated to be at temperatures higher than 300° C., preferably at 320° to 400° C., and under autogenous pressure, which will be close to 3000 pounds per sq. in. under the conditions. A batch process with a heating period of one hour is claimed. Oxygen is not fed to the emulsion but the autoclave is made sufficiently large to permit contained oxygen to act as the oxidant. Hence, the yield of phenol per batch operation is small, but as the benzene is not otherwise attacked, the conversion may be quite large.

Attempts have been made to utilize the tendency of phenol to polymerize in the presence of oxygen and caustic for the production of resins. Thus, 200 grams of phenol in six times the amount of 2.5 normal soda lye necessary to dissolve it, is heated for 2 hours at 200° C. under 40 atmospheres pressure and in the presence of air.[19] The air is passed through the solution and then through a cooler also under pressure. The blood red solution obtained in this way is acidified to yield resins and colors.

The results of these liquid phase experiments indicate that oxidations

[12] Friedel and Crafts, *Compt. rend.* 86, 884 (1878); *Ann. chim. phys.* (6) 14, 435 (1888).
[13] Radziszewski, *J. prakt. chim.* 23, 96 (1881); *Ann.* 203, 305 (1880).
[14] Hoppe-Seyler, *Ber.* 12, 1551 (1879), and Leeds, *ibid.* 14, 975 (1881).
[15] Nencki and Giacosa, *Z. physiol. chem.* 4, 339 (1880); Leeds, *Ber.* 14, 976 (1881); Nencki, *ibid.* 14, 1144 (1881).
[16] Leeds, *Ber.* 14, 1382 (1881).
[17] *Ber.* 33, 2015 (1900).
[18] Hale, U. S. Pat. 1,595,299 (1926) assr. to Dow Chem. Co.
[19] Brit. Pat. 149,979 (1921) Fischer.

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[14] Hoppe-Seyler, *Ber.* 12, 1551 (1879), and Leeds, *ibid.* 14, 975 (1881).
[16] Nencki and Giacosa, *Z. physiol. chem.* 4, 339 (1880); Leeds, *Ber.* 14, 976 (1881); Nencki, *ibid.* 14, 1144 (1881).
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[17] *Ber.* 33, 2015 (1900).
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[19] Brit. Pat. 149,979 (1921) Fischer.

of benzene to phenol in the vapor phase in the presence of catalysts might be practical, but as yet very little investigation has been recorded with that direct end in view. At the present time, phenol is manufactured on a commercial scale either (a) from coal-tar distillates by the application of various more or less involved methods of separation, (b) from benzene sulfonic acid by the usual method of fusion with alkali, or (c) hydrolysis of benzene halides.[20] References to other procedures describe the oxidation of benzene in the vapor phase, and are largely embodied in the patent literature.

One patent [21] has to do with the action of ozone at 390° C. in the presence of an oxygen-occluding substance such as platinum black or platinized asbestos. Pressure is said to exert an important influence and an appropriate form of apparatus is specified and illustrated. This patent is rather broad in its scope and contains fourteen claims covering the oxidation of turpentine and other substances as well.

A second patent [22] describes the production of phenol from benzene by mixing the same with oxides of nitrogen either alone or mixed with air. In the former case the oxides function as oxidizing agents and in the latter as catalysts. Any substance that will liberate the oxides of nitrogen under the conditions of the experiment may be used in place of the free oxides. Reactions between the substances in the mixture thus formed are effected by passing the same through a heated tube made of silica, porcelain or fire clay. In carrying out the process the vapor of the benzene is mixed with air by spraying or any other convenient device. The resulting mixture, or the air before coming in contact with the benzene, is mixed with oxides of nitrogen, by distilling nitric acid into the air stream or spraying it into the gaseous mixture and then decomposing the acid by electrical discharge or by other suitable device. The reaction chamber may or may not be filled with catalytic material such as aluminum oxide, zirconium oxide, etc. The gaseous mixture is heated preferably at 700° C. but this temperature may be varied over a wide range. After passing through a special form of apparatus designed for the experiment, the hot reaction gases are cooled to about 85° C. by circulating through a condenser at which stage the phenol separates. The remaining gas mixture after being enriched with benzene and oxides of nitrogen is recirculated. The phenol is separated from small amounts of the products such as naphthalene, diphenyl and phenylene oxide by distillation in a vacuum and can then be readily purified by recrystallization. Operation is conducted with a ratio of three volumes of air to one volume of benzene vapor and with nitric acid present to the extent of one per cent by weight of the benzene used. Yields are not given.

A patent [23] to the I. G. Farbenindustrie describes the preparation of

[20] a. Hale and Britton, *Ind. Eng. Chem.* 20, 114-24 (1928); b. U. S. Pat. 1,735,327 Lloyd and Kennedy to Federal Phosphorus Company; c. Brit. Pats. 288,308, 308,220-I. G. Farbenind.
[21] Brit. Pat. 2010 (1901) Wedge.
[22] U. S. Pat. 1,547,725 (1925) Bibb.
~ ~ ~ ~ Brit. Pat. 501,467 (1927) Schmidt and Roh.

phenol and halogenated phenols by the treatment of benzene or its halogen substitution products with oxygen in the vapor phase at temperatures of 400 to 500° C. and in the presence of oxides or oxygenated compounds of metals. Diluent gases may be used for the purpose of controlling the reaction.

Aromatic nitro compounds are claimed to be formed by passing aromatic hydrocarbon vapors in air over catalysts [24] formed by heating weakly basic metallic oxides, especially zinc or copper oxides, with nitrogen oxides. The preparation of nitrobenzene from benzene in this way is stated to occur at 290° to 300° C. A mixture of 11 per cent meta and 89 per cent ortho nitrotoluene is obtained from toluene. In connection with the use of nitrogen oxides, it should be noted that the nitration of phenols and quinones is accompanied by the evolution of hydrocyanic acid gas. This has been explained [25] by the formation of NO- derivatives, which are oxidized with rupture of the ring to give oximes of mesoxalic and dihydroxytartaric acids. These compounds decompose to give carbon dioxide, water, and hydrocyanic acid gas.

The fact that efficient conversion of benzene to phenol by air oxidation may have important industrial applications has led a number of investigators to attempt the conversion. However, yields have been low and in the case of liquid phase processes, generally accompanied by formation of tars and undesirable poly-hydroxylated derivatives. In the vapor phase catalytic oxidation of benzene with solid catalysts, Weiss and Downs [26] were able to obtain but 0.3 per cent yields of phenol on the basis of benzene charged. Yields on the basis of benzene converted were many times larger.

The presence of even this small an amount of phenol has some theoretical significance, however, since it indicates that phenol may be the initial oxidation product of benzene and shows that a hydroxylation mechanism similar to that postulated by Bone and his co-workers * may occur in aromatic oxidation. The presence of phenol as an initial oxidation product has been substantiated by the work of Bibb and Lucas,[27] who used nitric acid vapor as a homogeneous gas phase catalyst in the oxidation of benzene. These workers were able to obtain conversions of benzene to phenol as high as 52.4 per cent by passing a mixture of 156 liters of air, 299 grams of benzene, and 1.8 grams of nitric acid through a reactor at 690° to 710° C. with a time of contact in the neighborhood of 0.2 to 0.5 seconds. Yields as high as 5.6 per cent of phenol were obtained but at the expense of conversion which in this case was only 3.5 per cent.

The selective action of this vapor phase catalyst compared with the solid catalysts used by other workers in giving high conversions to the initial oxidation product, phenol, may be attributed largely to the fact that

[24] Ger. Pat. 207,170 (1908); *Chem. Zentr.* 1, 962 (1909).
[25] Seyervetz and Poizot, *Compt. rend.* 148, 286-8 (1909).
[26] Weiss and Downs, *J. Ind. Eng. Chem.* 12, 228 (1920).
* *Cf.* Chapter VI.
[27] Bibb and Lucas, *Ind. Eng. Chem.* 21, 635-8 (1929).

its action does occur in the gas phase. In the case of the solid catalysts the phenol would probably be more strongly adsorbed by the catalyst than the benzene due to its higher boiling point of 183° C. as against 80° C., as well as to its higher molecular weight, 94.08 as against 78.08, with the result that secondary oxidations and condensations would be prone to occur. In the case of the gas phase catalyst the phenol forms homogeneously throughout the reaction space and is swept out of the hot zone rather than forming just at the catalyst surface and being held as with solid catalysts.

The catalytic effect of the nitric acid gas has been attributed to (a) increase in the concentration of active oxygen and (b) greater oxidizing power of nitrogen peroxide.[27] The formation of phenol from benzene by electrochemical oxidation has been explained on the basis of atomic oxygen,[28] a hypothesis that may hold in this case. A mechanism for the catalytic effect of nitrogen peroxide based on the conclusion that it is readily activated by the absorption of radiation over a relatively wide range of frequencies is as follows:

$$NO_2 + h\mu = NO_2*$$
$$NO_2* = NO + O$$
$$O + benzene = phenol.$$
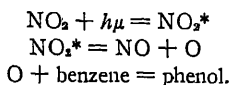
Or rather than dissociate into nitric oxide and oxygen the active nitrogen peroxide may react directly with benzene according to:

$$NO_2* + benzene = phenol + NO.$$
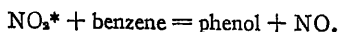
The nitric oxide may then recombine with oxygen to form the peroxide and the process be repeated.

$$2NO + O_2 = 2NO_2.$$
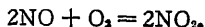
Secondary oxidation with a gas phase catalyst or electrolytic oxidation would result in the formation of dihydroxybenzenes:

$$phenol + O = C_6H_4(OH)_2.$$
$$\textit{dihydroxybenzene}$$
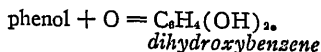
Continued oxidation would result in the formation of quinone from the para compound:

$$C_6H_4(OH)_2 + O = C_6H_4O_2 + H_2O.$$
$$\textit{quinol} \qquad \textit{quinone}$$
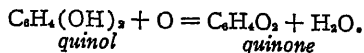
Both quinol and quinone have been found in the oxidation products of benzene.[26, 29]

Oxidation of the quinone would probably continue through the hydroxylation mechanism as follows:

[28] Fichter, *J. chim. phys.* **23**, 481 (1926).
[*] Active molecule.
[29] Fichter and Stocker, *Ber.* **47**, 2003 (1914).

enol   *keto*
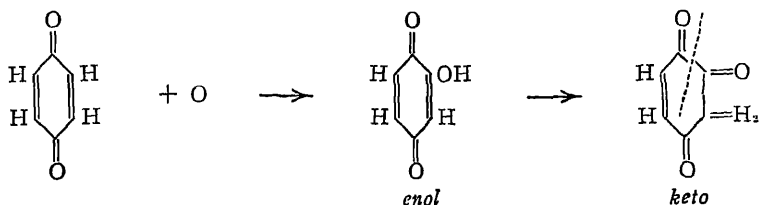
to form an unstable compound which, on re-arrangement and further oxidation, would result in the rupture of the ring to give maleic acid. Or the reaction might, however, be through oxidation at the double bond to give a dihydroxy derivative of quinone as in liquid phase oxidation: [80]
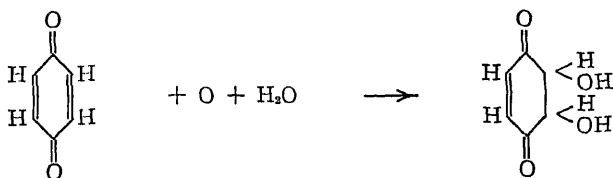
Continued oxidation would result in the formation of a polyketone followed by ring cleavage and formation of maleic acid, as in the case of the heterogeneous process.
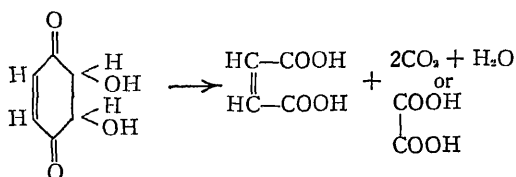
Or as in the case of the oxidation with silver peroxide in the liquid phase,[81] the ring may rupture without polyketones being formed.

The further oxidation of phenol may also result in the formation of catechol, $C_6H_4(OH)_2(1:2)$. The transformation may be effected by fusion with sodium hydroxide.[82] The substance may also be obtained by oxidizing benzene with hydrogen peroxide in the presence of ferrous sulfate [83] and by reducing o-benzoquinone with aqueous sulfurous acid in the cold.[84] Quinol may be prepared from phenol by oxidation with potassium persulfate in alkaline solution.[85] It can also be obtained directly from benzene by the electrolytic oxidation of an alcohol solution to which

[80] Terry and Milas, *J. Am. Chem. Soc.* 48, 2647 (1926).
[81] a. Kempf, *Ber.* 39, 3715 (1906); b. Pummerer and Rieche, *Ber.* 59B, 2161-75 (1926).
[82] Barth and Schreder, *Ber.* 12, 419 (1879).
[83] Cross, Bevan and Heiberg, *Ber.* 33, 2018 (1900).
[84] Willstätter and Pfannenstiel, *Ber.* 37, 4744 (1905).
[85] Ger. Pat. 81,068.

a small quantity of sulfuric acid has been added;[36] and from p-benzo-quinone by a variety of different methods of reduction.[37]

Catechol is transformed into o-benzoquinone by suspending its lead salt in chloroform and then treating the mixture with iodine.[38] Quinol is readily transformed into the corresponding p-benzoquinone by sudden heating above its point of sublimation.[39] In this case, quinhydrone, an addition product of quinol and quinone ($C_6H_4O_2 . C_6H_6O_2$) is also formed. The same transformation occurs when quinol is heated in a closed vessel,[40] when its vapor is passed through a glowing tube,[41] and when treated in the liquid phase with a great variety of reagents. In the latter case, quin-hydrone is frequently formed. Para-benzoquinone may also be prepared directly from benzene by various methods of oxidation[42] and also from phenol.[43] In the latter case an addition product between phenol and quinone is formed, namely, phenoquinone ($C_6H_4O_2 . 2C_6H_6O$).

Although the price of phenol has fallen considerably since the war, a fact indicating largely the efficiency of the newer process of chlorbenzene hydrolysis, and also due to improvements in the sulfonation of benzene and the fusion of sodium benzene sulfonate, it is possible that the "ideal" process of direct oxidation may yet be developed to give a still lower price. A price lower than the present should stimulate further the already large demand for phenol and for its reaction products such as resins, and even open up new fields for use, a possibility of great promise in the case of synthetic resins.

Oxidations Involving Ring Cleavage

Oxidations which involve an opening up of the benzene ring were first observed in connection with investigations in the liquid phase. As early as 1870 Carius studied the behavior of aromatic compounds under the action of "hydrated chloric acid" which was obtained by treating potassium chlorate with sulfuric acid and then freeing the mixture from perchloric acid. In the case of benzene, the main product of the reaction consisted of a substance[44] to which Carius gave the name of "trichloro-phenomalonic acid." The latter, when heated with concentrated hydrogen iodide was reduced to give succinic acid and when warmed with baryta water decomposed to give phenaconic acid.[45] The constitution of "tri-

[36] Gattermann and Freidrichs, *Ber.* 27, 1942 (1894).
[37] Grandmougen, *Ber.* 39, 3561 (1907); Ger. Pat. 168,273 (1906) Höchster Farbwerk; Sabatier and Mailhe, *Compt. rend.* 146, 457 (1908); *Ann. chim. phys.* (8) 16, 88 (1909).
[39] Jackson and Koch, *Ber.* 31, 1458 (1898); *Am. Chem. J.* 26, 21 (1901); *compare also* Willstätter and Müller, *Ber.* 41, 2580 (1908).
[30] Wöhler, *Ann.* 51, 153 (1844); *compare* Hesse, *Ann.* 200, 242 (1879).
[40] Hartley and Leonard, *J. Chem. Soc.* 95, 49 (1909).
[41] Hesse, *Ann.* 114, 297 (1860).
[42] Kempf, *Ber.* 38, 3963 (1905); Ger. Pat. 189,178 (1902) Walter Lang; Ger. Pat. 117,251 (1901) Kempf; *compare Centralblatt* 1901, I, 248.
[43] Wichelhaus, *Ber.* 5, 248 (1872); *also* Kempf and Moehrke, Ger. Pat. 256,034 (1913); *Ber.* 47, 2620 (1914).
[44] *Ann.* 155, 217-33 (1870); *compare also ibid.* 140, 317 (1866); 142, 129 (1867); 143, 319 (1867); 149, 257 (1869).
[45] Later identified as fumaric acid. *Compare* Zincke, *Ber.* 4, 298 (1871).

chlorophenomalonic acid" was the subject of controversy [46] until 1884, when it was definitely identified by Kekulé as β-trichloroacetoacrylic acid, $(CCl_3COCH = CHCOOH)$.[47] In repeating the work of Carius, Kekulé found that slight variations in the conditions of the experiment had a very great influence upon the results. The mechanism of the reaction was explained by supposing that simultaneous oxidation and chlorination of benzene leads to the formation of a large number of intermediate compounds, viz., chlorinated benzene, phenol, chlorinated phenols, quinones and finally chlorinated quinones. Of these, chlorinated quinone is probably to be regarded as the parent substance of "trichlorophenomalonic acid," since its simultaneous chlorination and oxidation would account in a comparatively simple manner for the formation of the latter substance:
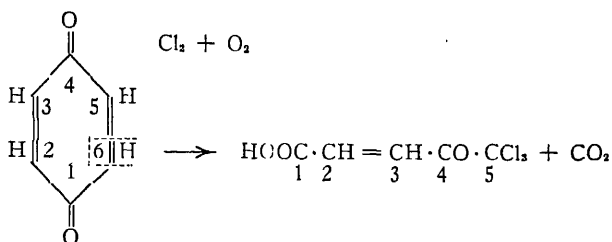
The work of Kekulé confirmed the results described by Carius in that he found that "trichlorophenomalonic acid" was actually formed when the directions given by Carius were exactly followed. The substance so obtained agreed in all respects with that described by the earlier investigator, except for the fact that when decomposed with warm baryta water it was observed to give chloroform and maleic instead of fumaric acid.

The questions raised by Kekulé's interpretation of the mechanism of this reaction led to a number of investigations which involved a further study of the oxidation of aromatic phenols and quinones. Thus, for example, Zincke in collaboration with Kuster [48] and Rabinowitch [49] undertook a systematic investigation of the action of chlorine (potassium chlorate plus hydrochloric acid) on various derivatives of the three dihydroxybenzenes. The results of these experiments showed that these classes of benzene derivatives split up under conditions to give aliphatic compounds. The intermediate compounds which were formed from tetrahydrobenzene during these transformations, were identified as the hexachloro-o-diketone derivative (I) and the pentachloro-m-diketone derivative (II).

[46] Krafft, *Ber.* 10, 797 (1877).
[47] Kekulé and Strecker, *Ann.* 223, 179-197 (1884).
[48] *Ber.* 21, 2719 (1888); 22, 486 (1889); 23, 812, 2200 (1890); 26, 2184 (1893); 27, 3364 (1894).
[49] *Ber.* 23, 3766 (1890); 24, 912 (1891).

$$\text{(I)} \qquad\qquad \text{(II)}$$
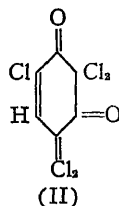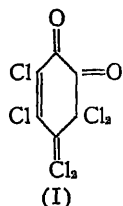
Also, chlorine was found to convert o-benzoquinone into tetrachloro-o-quinone.

To cite another of the many possible examples, tetrachloro-p-quinone (chloranil) is transformed under similar conditions to give the hexachloro-p-diketone derivative (III). Hydrolysis of this para derivative with caustic soda caused the ring to break with formation of dichlormaleic acid, trichloroethylene, and sodium chloride as follows:

$$\text{(III)}$$

$$
\begin{array}{c}
\text{COOH} \\
\text{CCl} \\
\text{CCl} \\
\text{COOH}
\end{array}
\; + \;
\begin{array}{c}
\text{CCl}_2 \\
\text{HCCl}
\end{array}
\; + \; \text{HCl}
$$

$$\downarrow + \text{NaOH}$$

$$\text{NaCl} + \text{H}_2\text{O}.$$
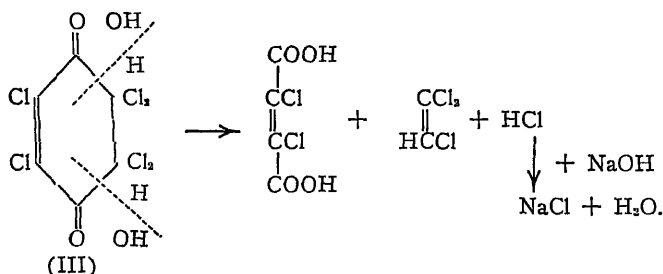
It was observed, moreover, that in all cases the splitting of the benzene ring took place between a CO and a CCl_2 group in the chlorinated keto-derivative.[50]

The cleavage of the benzene ring by means of chlorine in alkaline solution has been further investigated by Hantzsch. This work has been summarized in the form of tabular statements which indicate the transformation of the various substances into chlorinated keto-derivatives and ultimately into cyclopentenes and their decomposition products.[51]

The oxidation of phenol by means of potassium permanganate has been studied by Döbner.[52] In as much as the product proved in this case to be meso-tartaric acid, it seems probable that hydroquinone, quinone and maleic acid may have been formed as intermediate products,[53] particularly in view of the fact that the latter when oxidized with potassium permanganate is known to yield inactive tartaric acid.[54]

Cleavages of the ring which result from the action of alkaline reducing agents have proved to be much less drastic than simultaneous chlorinations

[50] a. *Ber.* **27**, 3364 (1894); b. Zincke and Fuchs, *Ann.* **267**, 1 (1892); *compare also Ber.* **23**, 1706 (1890).
[51] *Ber.* **22**, 1243, 1252 and 2853 (1889); *also Ber.* **25**, 827 and 843 (1892).
[52] *Ber.* **24**, 1753 (1891).
[53] Kempf, *Ber.* **39**, 3718 (1906).
[54] *Compare* Kekulé and Anschutz, *Ber.* **13**, 2150 (1880); **14**, 713 (1881); *Ann.* **221**, 230 (1883).

and oxidations.[55] The two types of transformations are, nevertheless, very closely analogous as will be apparent from the following sample:[56]

cyclohexane-1: 3-dione   γ acetyl-butyric acid
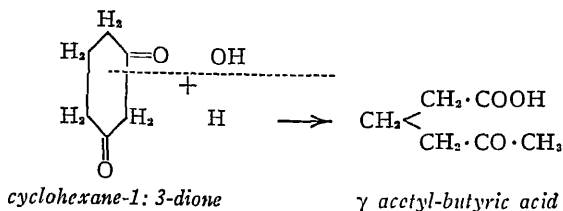
The mechanism of the transformations involved in the formation of maleic acid from benzene in the liquid phase has been taken up in considerable detail in two papers by Kempf.[57] While the second of these is largely theoretical in character, it is of extreme interest and affords a basis for valuable lines of speculation. In this connection it may be noted that derivatives of other heterocyclic ring compounds, such as furfurane, thiophene and pyrrol, likewise yield derivatives of maleic acid on oxidation.[58] Attention may also be called to the fact that ketonic hydrolysis of the same general type as that met with in cleavages of the benzene ring are of fairly frequent occurrence. For example, acetone under the action of light is hydrolyzed to give acetic acid and methane [59] and acetylacetone is readily decomposed by boiling with water into acetic acid and acetone.[60]

Attempts have been made at commercial utilization of the relationships which have been established in this way between benzene and its derivatives on the one hand and their different cleavage products on the other hand. Thus, for example, patents issued to the Farbenfabrik v. F. Bayer and Company [61] describe the preparation of methyl adipic acid from methyl cyclohexanol and methyl cyclohexanone respectively by liquid phase oxidation using nitric acid and alkaline potassium permanganate successively. This affords a striking illustration of the fact that the benzene ring may be split without loss of any of its carbon atoms. Indeed cyclohexene itself (alone or diluted with acetone) may be oxidized by agitation with oxygen in the presence of osmium (or tellurium) to give adipic acid along with small quantities of adipinaldehyde, cyclohexanol, etc.[62] The slow oxidation of cyclohexene has been indicated to occur through the formation of a peroxide.[63]

[55] *Compare* Einhorn and Willstätter, *Ber.* 28, 744 (1895); Merling, *Ann.* 278, 32 (1893).
[56] Vorländer, *Ber.* 28, 2348 (1895).
[57] *Ber.* 38, 3963 (1905); 39, 3715 (1906).
[58] Ciamician and Silber, *Ber.* 20, 698, 2594 (1887); Ciamician and Angeli, *Ber.* 24, 77, 1347 (1891).
[59] Ciamician and Silber, *Ber.* 36, 1582 (1903); 40, 2415 (1907).
[60] Knoevenagel and Arndts, *Ber.* 35, 1983 (1902); see also *Ann.* 190, 276 (1877). For other examples of the hydrolytic decomposition of hydro-aromatic ketones under the action of light consult *Ber.* 40, 2419 (1907); 41, 1071, 1928 (1908); 42, 1510 (1909).
[61] Ger. Pat. 221,849 (1908); French Pat. 409,083 (1908); Brit. Pat. 24,298 (1909).
[62] a. Willstätter and Sonnenfeld, *Ber.* 46, 2952-58 (1913); b. Schrauth, *Chem. Ztg.* 53, 41-43 (1929).
[63] Zelinskii and Borisov, *Ber.* 63B, 2362-5 (1930).

Further experimentation by the Farbenfabrik v. F. Bayer and Company led to the very important discovery that cyclohexane and its derivatives could be incompletely converted to butadiene, a most valuable technical product.[64] The process in this case is carried out in the vapor phase and consists in passing the vapors of cyclohexane in a current of carbon dioxide (after preheating at a suitable temperature) over a catalyst such as lead, carbon, quartz, aluminum silicate, etc., maintained electrically at a dark red heat. The butadiene is removed by condensation or by passing the gaseous product through bromine and then separating the butadiene tetrabromide by a process of distillation and fractional crystallization.[65] Direct cracking of cyclohexane has been shown to yield quantities of butadiene when high temperatures are used.[66] Other methods for preparing butadiene have been described in some detail by Ostromisslinski [67] in connection with a study of the action of high temperatures upon aromatic hydrocarbons.

It will be noted that in all of the cases which have been described thus far, cleavage of the benzene ring takes place only after the six valencies of the ring carbon atoms have been saturated by the addition of chlorine or hydrogen and that for the most part such oxidations have been studied only in the liquid phase.

The first important investigation of the phenomena involved in the oxidation of benzene itself, in the vapor phase, was undertaken by Orloff in 1908.[68] This work was undertaken in conjunction with Orloff's study of the oxidation of the alcohols which has already been referred to in some detail.[69] His work on the oxidation of the hydrocarbons was, unfortunately, merely preliminary in character. He was concerned mainly with the oxidation of Baku petroleum but also gave some time to the study of benzene and toluene. Using a copper sieve contact mass, he succeeded in oxidizing toluene to benzaldehyde. In the case of benzene he obtained a number of different oxidation products most of which he was unable to identify.

More recently the problem of the oxidation of the aromatic hydrocarbons has been investigated by Gibbs and his associates, working at the Bureau of Chemistry in Washington, and by Weiss and Downs with their associates, working in the laboratories of the Barrett Company at Edgewater, New Jersey. These respective investigations are said to have paralleled each other to a large extent and in some instance to have even duplicated each other. The Bureau of Chemistry has published very few details of this work but American and foreign patents have appeared

[64] Ger. Pat. 278,647 (1912).
[65] *Ann.* 308, 337 (1899).
[66] a. Brit. Pat. 307,945 (1927) I.G. Farbenind; *compare* b. Frolich, Simard and White, *Ind. Eng. Chem.* 22, 240 (1930).
[67] *J. Russ. Phys. Chem. Soc.* 47, 1472-94; 1947-78 (1915).
[68] *J. Russ. Phys. Chem. Soc.* 39, 855, 1023, 1414 (1907); 40, 652, 659, 796, 799, 1590, 1596 (1908); *Z. physik. Chem.* 69, 499-505 (1909).
[69] "Formaldehyde: "Der bisherige Stand der wissenschaftlichen Erkenntnis und der technischen Verwendung sowie neue Untersuchungen über seine Herstellung und über pyrogenetische Kontactreaktionen," translated into German by C. Kietaibl Barth, Leipzig, 1909.

which describe the production of phthalic anhydride from naphthalene, anthraquinone from anthracene, phenanthraquinone from phenanthrene and benzaldehyde from toluene.[70] Specific processes involving the use of different catalysts at different conditions of temperature and pressure are described in the carrying out of the above reactions but very little of an exact nature has been recorded.

The investigations of Weiss and Downs, while dealing with all of the above types of oxidation reactions, concentrated much more specifically upon the oxidation of benzene itself in the vapor phase. This work was extended over a considerable period of time and was crowned by the actual production of maleic and fumaric acids on a commercial scale. The different phases of these investigations have been marked from time to time by the appearance of various American and foreign patents. However, the information which has been made public in this way has not been further supplemented by as detailed an account of the general method used by these investigators in their approach to the specific problem of the oxidation of benzene as would be desirable.[26] In general, it may be said that the products which have been obtained by the oxidation of benzene under various conditions consist of phenol, diphenyl, quinone, and maleic acid.

In the formation of valuable oxygen-containing compounds by the controlled or partial oxidation of hydrocarbons, such as benzene, two factors are of great importance, i.e., temperature and type of catalyst. Other factors such as composition of hydrocarbon-air mixture and time of contact are also important. All of these factors are intimately related to each other and the successful operation of the process depends upon the control of each of them. It was early found that if mixtures of benzene vapor and air in excess of that necessary for complete combustion were passed through heated tubes of such non-catalytic materials as iron, silica, aluminum, etc., and the temperature allowed to rise at will, only complete combustion products could be obtained, and no intermediate oxidation products could be isolated. On the other hand, if such mixtures of benzene vapor and air were passed over a catalyst such as platinum black, complete combustion also occurred but at a temperature far below that necessary in the empty tube made of non-catalytic material. However, only very small amounts of intermediate products could be obtained with such an active catalyst even when the temperatures were carefully controlled or the time of contact made very short. It is difficult to form any definite idea as to the temperatures which were actually attained by the reacting gases in most of the early experiments reported in the literature. Lack of uniformity in construction of reaction chambers, in displacement of cata-

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[70] Brit. Pat. 14,150 (1917); 14,151 (1917); Canadian Pat. 186,444 (1918); 186,445 (1918); U. S. Pats. 1,284,887 (1918); 1,284,888 (1918); 1,285,117 (1918); 1,288,431 (1918); 1,303,168 (1919), and others.
[26] Weiss and Downs, *J. Ind. Eng. Chem.* **12,** 228 (1920).

lyst, and especially· in· method of measuring and reporting temperatures leaves much of the reported information open to doubt.

It has been found, however, that there exist a number of catalytic materials, notably the oxides of the metals comprising the fifth and sixth groups of the periodic system, which enable intermediate oxidation products to be isolated under carefully controlled temperature and time of contact conditions. There is, for instance, a very definite temperature range within which maximum yields of maleic anhydride may be obtained by the oxidation of benzene in the presence of such catalysts as vanadium oxide. At temperatures as low as 100° C. this catalyst is without activity in promoting oxidation,[71] at 300° C. it is becoming active, and at 400° to 500° C. reaches its optimum capacity in the production of maleic anhydride. At higher temperatures complete combustion products predominate. The advantage of such catalysts over the more active materials as platinum or ceria is that the temperature range in which partially oxidized products may be isolated is much wider. This makes it possible for the process to be operated on a commercial scale, whereas if catalysts such as platinum are used the temperature range between the point at which oxidation starts at an appreciable rate and that at which complete oxidation products result is extremely narrow so that even if the mechanism be the same no intermediate products can be isolated on·a large scale.

A great variety of catalysts have been patented for use in the vapor phase oxidation of benzene to maleic anhydride or acid. Oxides of the metals of the fifth and sixth groups of the periodic system or mixtures of these oxides have been particularly stressed. Vanadium pentoxide has been studied more in this connection than other oxides because of its more powerful action in causing the oxidation of benzene without causing complete combustion, and is claimed as a catalyst either alone or in mixtures in a number of patents.[72] Multicomponent zeolites made by reacting at least one soluble silicate, one metallate, and one metal salt, the basic radical of which enters the non-exchangeable nucleus of the zeolite have been claimed for the vapor phase oxidation of various aromatic compounds [73] including benzene. For improved heat transfer and consequent better temperature control attempts have been made to use metals as supports for the active catalytic material. Aluminum turnings, or particles with rough surfaces are coated with oxides of vanadium or molybdenum and the coated particles then carefully packed into the narrow reaction tubes.[74]

[71] Downs, *J. Soc. Chem. Ind.* **45T**, 189 (1926).

[72] a. Craver, U. S. Pat. 1,636,857 (1927), mixtures of at least two oxides of 5th and 6th groups of periodic system; b. Weiss and Downs, U. S. Pat. 1,318,631, 1,318,632, 1,318,633 (1919); c. Meigs and Ellis, U. S. Pat. 1,486,781 (1924), complex salts such as chromium vanadate, cobalt molybdate, nickel vanadate.

[73] a. Jaeger, Brit. Pat. 296,071 (1927) to Selden Co. *See also* b. Jaeger, Brit. Pat. 291,419 (1927) to Selden Co.

[74] Downs, U. S. Pat. 1,672,308 (1928); Brit. Pat. 153,877 (1920) to the Barrett Co.; *see also* Chapter I.

The catalysts that have been found to be particularly effective in this oxidation, principally the oxides of vanadium and molybdenum or mixtures, are of the type capable of forming a series of oxides by changes in valence of the metal atom. Suggestive experiments have been made [75] which indicate that the peculiar effects, obtainable in the partial oxidation of benzene with such catalysts are due to valence changes occurring during the reaction between oxygen and hydrocarbon. The behavior of the vanadium oxide catalyst indicates that the mechanism of the catalytic action might involve an oscillation between V_2O_5 and V_2O_4, which, if true, would introduce another rate factor in the oxidation, i.e., the rate at which such oscillations occur. Whether or not this rate is controlling will depend on the relative rates of the other factors involved.

Investigations purporting to disclose the mechanism of the vapor phase oxidation of benzene in the presence of solid catalysts have of necessity been complicated by the many variables affecting the reaction as, composition of mixture, physical and chemical character of catalysts, temperature, pressure, time of contact, presence of diluent gases and water vapor, secondary side reactions, etc. Nevertheless, mechanisms have been proposed for the reaction based on the results obtained from actual experiments. The main reactions are probably: benzene to quinone to maleic acid to complete combustion products.[26] However, the complete combustion of a molecule of benzene to water and carbon dioxide requires fifteen atoms of oxygen, thus making possible a very complex mechanism involving a possibility of fifteen oxidation steps, a rupture of the ring step, and several rearrangement and decomposition steps, besides the complicating polymerization and condensation side reactions.

FIG. 35.—Change in catalyst composition with oxygen-benzene ratio at 400° C.[75]

The fact that Weiss and Downs have been able to isolate phenol in the products of their reactions with solid catalysts indicates a hydroxylation mechanism similar to that postulated in the case of vapor phase catalysis, in which the formation of the monohydroxylated derivative is the first step. The presence of the hydroxyl group as a substituent in the benzene molecule activates the para and ortho positions so that the introduction of a second oxygen molecule would be expected to result in the formation of quinol $(C_6H_4(OH)_2 1:4)$ and catechol $(C_6H_4(OH)_2 1:2)$ with a preponderance of the former. Quinone which would result from the further oxidation of quinol has been found in the oxidation products from benzene for the case of the homogeneous catalytic reaction.

[75] Weiss, Downs and Burns, *Ind. Eng. Chem.* **15**, 965 (1923).

Indeed, it has been found [26, 70] that under the conditions of the experiments, the proportion of quinone to maleic acid remains fixed and is not materially altered by introduction of quinone with benzene. However, the proportion of quinone is never large in the case where solid catalysts are used. The mechanism of the further oxidation of quinone to maleic anhydride is somewhat speculative since the isolation of any of the intermediate compounds in this step has not been reported in the vapor phase oxidation experiments. However, the formation of a poly-ketone by the following reactions seems a possibility since it may be assumed that a continuation of the hydroxylation process followed by the molecular rearrangement, would be expected.

enol   *keto*
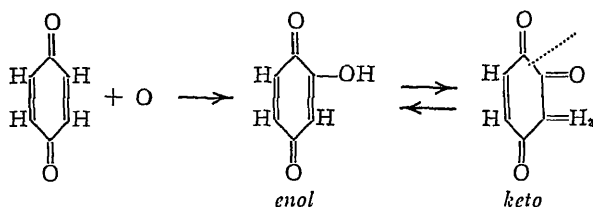
The continued oxidation of this product finally results in rupture of the ring and formation of maleic anhydride. During the cooling and con-

maleic anhydride
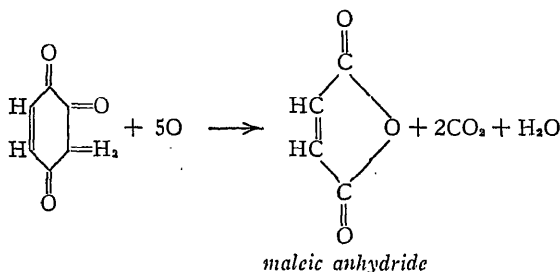
densation of the products some of the anhydride is converted to maleic acid by the water formed during the oxidation or added for cooling purposes.

maleic anhydride   *maleic acid*

[70] U. S. Pat. 1,318,631 (1919).
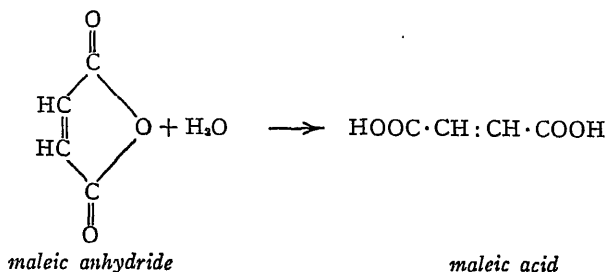
Further oxidation of the maleic acid or anhydride results in comp. a combustion as far as reported results show. However, Weiss and Down were able to identify definite amounts of formaldehyde in their product, formed presumably by side reactions involving decomposition of the intermediates or continued oxidation of the product.

Yields of 60 pounds of maleic acid per 100 pounds of benzene consumed may be obtained.[77] Catalyst life is comparable with that realized in the oxidation of naphthalene to phthalic anhydride where 20,000 times the weight of the catalyst of phthalic anhydride may be obtained in continuous operation before it is necessary to replace or revivify the catalyst.

The reaction of benzene with oxygen to form maleic acid is highly exothermic and large quantities of heat must be removed from the reaction zone. Special means must be provided for the removal of this heat to prevent the overheating of the catalyst mass and consequent complete combustion of the hydrocarbon. This removal of the heat of reaction constitutes a major problem in the industrialization of the process and will be discussed more fully in a later section.

TABLE XXXV.—*Heats of Combustion* [78] (*products are liquid water and gaseous carbon dioxide*).

	Kg. cal./ mol.	Kg. cal./ gm.	B.t.u./ lb.	Molecular Weight
Benzene (liq.)	783.4	10.04	18,095	78.08
Quinone (solid)	656.5	6.075	10,930	108.08
Maleic acid (solid)	326.1	2.812	5,060	116.05

TABLE XXXVI.—*Heats of Oxidation* (*from heats of combustion*).

	Kg. cal./ mol.	B.t.u./lb. Benzene	Atoms O Involved	B.t.u./atom O Reacted
Benzene to quinone	126.9	2925	3	975
Quinone to maleic acid........	330.4	7628	6	1271
Maleic acid to $CO_2 + H_2O$....	326.1	7540	6	1257

Therefore, the heat theoretically liberated in the oxidation of benzene to maleic acid is 10,553 B.t.u. per pound of benzene reacting and the heat liberated in the complete combustion of benzene is 18,093 B.t.u. per pound. In practice, where 40 per cent of the benzene may undergo complete combustion the heat liberated is, therefore, the weighted average of these two quantities. Since the oxidation reactions of organic substances, such as the oxidation of benzene to maleic acid, are substantially non-reversing reactions, it is not possible to adjust the temperature of the reaction chamber to obtain a high rate of conversion at a high temperature in the first part and a slower rate at a lower temperature to complete the reaction in the latter part as is done in the case of the oxidation of sulfur dioxide to sulfur trioxide.

While maleic acid does not have the volume demand of such oxidation

[77] Weiss and Downs, *J. Soc. Chem. Ind.* **45T**, 193 (1926).
[78] Kharasch, *Bur. Standards J. Research* **2**, February (1929).

products as phthalic anhydride, anthraquinone, benzaldehyde, or benzoic acid, a number of uses and conversion products have been developed or proposed. Maleic acid may be converted to malic acid with theoretical yields by autoclaving in aqueous solution. The malic acid is marketed as such as a substitute for citric or tartaric acids for use as an organic acidulant.[70a] The sodium salt of malic acid is being sold for use in salting food by persons who cannot use sodium chloride.[70b] Maleic or fumaric acid is converted to succinic acid by reduction. This reduction may be accomplished by (1) hydrogenation of the sodium acid salt of either maleic or fumaric acid in the presence of a nickel catalyst or (2) by electrolytic reduction. Succinic acid is being used in the development of resins having certain marked advantages over the phthalic anhydride resins, such as resistance to shock, good color, and permanency.[80] Other uses include the formation of esters and condensation products which may become of considerable industrial importance.[81] Maleic anhydride is being used in the manufacture of synthetic resins which are being used in constantly increasing amounts in the formulation of varnishes.

The study of the formation of the polyesters from dibasic acids and glycols has been undertaken from the theoretical standpoint by Carothers and his collaborators as well as by a number of other workers.[82] As an example of the type of reaction, the action of succinic acid on ethylene glycol may be considered. In the presence of a slight excess of glycol, esterification proceeds rapidly at a temperature of 160° to 175° C. with elimination of water. When excess glycol is removed at 1 mm. of mercury pressure and 220° to 250° C., a very viscous liquid remains in the hot flask. When cool, the product is a hard, brittle, opaque, white mass of high molecular weight. Modifications of the reaction conditions or of reactants give rise to modified products of the same general character.

Oxidation of Derivatives Containing Side Chains

The oxidation of aromatic hydrocarbons containing an aromatic nucleus and one or more aliphatic side chains may be readily effected without any very appreciable rupture of the ring itself. Under specified conditions such oxidations may be so controlled as to give satisfactory yields of the desired oxidation products, but in most cases investigations in this field have been covered by patents. An historical survey of the somewhat meager information on the subject afforded by the literature will afford a background.

In 1873, Coquillon [83] passed a mixture of air and toluene vapor through a tube containing an incandescent platinum wire and was able to identify benzaldehyde as one of the products of oxidation. In a subsequent re-

[79] a. Weiss, Downs, and Corson, *Ind. Eng. Chem.* 15, 628 (1923); b. Weiss and Downs, *J. Am. Chem. Soc.* 45, No. 10 (1923).
[80] U. S. Pats. 1,091,732, 1,091,627-8, 1,108,329-32, 1,413,144-5, 1,489,744, 1,424,137 and others.
[81] Bailey and Boettner, *Ind. Eng. Chem.* 13, 905 (1921).
[82] Carothers, *Chem. Rev.* 8, 361 (1931) discusses these experiments collectively.
[83] *Compt. rend.* 77, 444-46 (1873).

port [84] the same investigator recommended palladium as representing a better catalyst than platinum in operations involving the partial oxidation of aromatic hydrocarbons. A few years later Walter [85] modified the experiment by substituting other catalysts. By using the same general form of apparatus as that described by Tollens [86] and employing a copper spiral as catalyst, he succeeded in preparing benzaldehyde by oxidizing a mixture of toluene vapor and air. The same results were obtained by employing as a catalyst asbestos which had been saturated with a solution of ammonium vanadate and then ignited. With the vanadium pentoxide catalysts he was able to obtain a yield of 5.7 per cent of benzaldehyde and benzoic acid from the toluene-air mixture.

In 1907, Woog [87] passed air through toluene which was heated on a liquid bath to a temperature of 80° to 100° C. The mixed vapors were then conducted through a contact tube 55 to 60 cm. long and 25 to 30 mm. in diameter, and drawn out at its further end into a section 20 cm. long which was adapted to serve as a condenser. The tube itself was heated electrically by means of a resistance wire wound around it. Experiments were made with catalysts consisting of finely divided platinum at a temperature of incandescence and with oxides of iron, nickel, copper and manganese deposited on pumice. In the preparation of the latter, powdered calcined pumice stone was thoroughly incorporated with a paste of the pure oxide of the metal, drying and stirring according to the method which has been described by Brunel.[88] Toluene was said to be completely converted into benzaldehyde by iron oxide at 175° to 300° C. and by nickel oxide at 150° C. It was partially oxidized by copper oxide at 180° to 260° C., and completely oxidized by manganese dioxide at incandescence, while with porous carbon at 370° C., it was converted into benzoic acid without incandescence of the contact mass. The best yields of benzaldehyde (20 per cent) were obtained when toluene was heated at 90° C. and its vapor mixed with air passed over an iron catalyst heated at 280° C. In the case of all of the metallic oxides incandescence was set up at temperatures between 250° and 300° C. In a patent [89] taken out at about the same time, minor modifications of the above procedure are described. It is stated, for example, that better results may be obtained by heating the gases issuing from the contact chamber at a temperature above the boiling point of benzaldehyde since under these conditions the benzaldehyde is more readily condensed in the condenser into which they then pass, and instead of passing a current of air through toluene, the air may be passed directly into the catalyst chamber together with liquid toluene which is then immediately vaporized. Carbon dioxide and nitrogen may also be added to the air to act as diluents in controlling the reactions.

[84] *Ibid.* **80**, 1089-90 (1875).
[85] *J. prakt. Chem.* **51**, 107-11 (1892); *see also* Brit. Pat. 21,941 (1905) Walter.
[86] *Ber.* **19**, 2133 (1886).
[87] *Compt. rend.* **145**, 124-26 (1907).
[88] *Ann. chim. phys.* (8), **6**, 205 (1905).
[89] French Pat. 379,715 (1907) Chavy, Delage and Woog.

Somewhat later a patent issued to Lowenthal [90] described the oxidation of aromatic hydrocarbons or alcohols to aldehydes by the action of oxygen or oxygen containing gases in the presence of a contact substance consisting of the residue resulting from the reduction of the salts of chromic acid with volatile bases. For example, the contact mass may be obtained by moistening ammonium chromate with methyl alcohol and then igniting. Another patent [91] proposes the use of vanadic or molybdic acids or the vanadates and arsenates of copper, silver, lead, thorium, platinum, cerium, nickel and cobalt as catalysts which are suitable for the oxidation of side chains present in aromatic hydrocarbons.

In 1918, the Selden Company, Inc., in Delaware, embodied the following claims in two patents: [92]

First: The oxidation of the side chains of aromatic hydrocarbons and of the lower oxidation products of such hydrocarbons (including light hydrocarbons obtained by the cleavage of heavy hydrocarbons) by passing their vapors mixed with air or oxygen (the latter in an excess equal to about twice that required by theory) over catalysts consisting of metals of the fifth and sixth groups of the periodic system, preferably the oxides of vanadium and molybdenum, but also including chromium, uranium, tungsten, antimony and bismuth in fine or coarse physical condition and used singly or in the form of mixtures. The temperature range given is 200° to 500° C. preferably 350° to 450° C., for the reacting gases but the catalyst may have a higher temperature, the difference between these two depending upon the concentration of the reacting gases, the rate of flow, the physical condition of the catalyst and other factors. The example cites the oxidation of toluene by use of vanadium pentoxide and provides for the separation of toluene from benzaldehyde and benzoic acid in the reaction product by suitable chemical methods such as the addition of sulfite, the formation of salts of the acid, etc.

Second: The oxidation of aromatic nuclei with a plurality of chains or with a ring at two points of said nucleus, or of the lower oxidation products of such hydrocarbons (including light hydrocarbons obtained by cleavage). The conditions are practically the same as in the preceding case, viz., a temperature of 250° to 600° C. for the reacting gases; the same catalysts but supported on carriers; and the mixed vapors passed over or through the catalysts. The examples include the oxidation of xylene, naphthalene and anthracene which in all cases results in formation of a mixture of typical oxidation products.

Canadian patents [93] taken out by Gibbs in the same year describe the same processes while a later United States patent assigned to the Government by Gibbs [94] and which may be mentioned in this connection, describes, in particular, methods for the preparation of a catalyst from vanadium oxide which is useful in promoting various oxidation reactions.

Patents by the Barrett Company [95] have been issued which describe similar oxidation processes with special emphasis upon conditions such as to preclude the formation of acid products in any but negligible amounts. The first of these patents relates to the production of practically pure

[90] Ger. Pat. 239,651 (1909) Lowenthal.
[91] Brit. Pat. 156,244 and 156,245 (1916) Wohl.
[92] Brit. Pat. 119,517 and 119,518 (1917) Gibbs assr. to the Selden Co.; *see also* U. S. Pat. 1,284,887 (1918) Gibbs to the people.
[93] Can. Pat. 186,444 and 186,445 (1918) Gibbs; *also* Gibbs, U. S. Pat. 1,417,367 (1922); 1,444,068 (1923).
[94] U. S. Pat. 1,458,478 (1923) Gibbs assr. to U. S. Govt.
[95] U. S. Pat. 1,321,959 (1919) Weiss and Downs assrs. to the Barrett Co.

benzaldehyde with water as a by-product and describes the oxidation of commercial toluene. This is vaporized in any convenient way and then mixed with oxygen containing gases, viz., oxygen or ozone or air or a mixture of any of these together with a blanketing or diluent gas in order more readily to control the reaction. The catalyst consists of molybdenum oxide distributed on a suitable carrier such as asbestos, pumice, etc. This is distributed in a tube which may be heated at about 500° C. under atmospheric pressures or as high as 700° C. under decreased pressures. After the separation of benzaldehyde the reaction gases containing unreacted toluene are suitably enriched and recirculated. The best results were obtained by using a mixture containing air and toluene vapors in approximately equal proportions and passing this over a catalyst of molybdenum oxide at a temperature slightly above 500° C. at atmospheric pressure. At temperatures below 500° C. only small yields of benzaldehyde are obtained. Whereas other catalysts will produce benzaldehyde in the reaction products mixed with other oxygenated products, molybdenum oxide permits the reaction to occur almost exclusively to benzaldehyde and water. Confirmation of these claims is not to be found in the periodical literature. By using molybdenum oxide as a catalyst with pumice support, Kusnetzov and Stepanenko [96] were able to oxidize 26.32 grams of toluene so that 7.1 grams went to benzaldehyde, 0.12 grams went to benzoic acid, 7.0 grams to carbon dioxide, and 12.1 grams to carbon monoxide.

A later improvement of the above process [97] discusses the various effects which may be produced upon the reaction by the action of different combinations of metals which may be used as catalysts, preference being given to a mixture of the oxides of uranium and copper with molybdenum oxide as affording the best yields of relatively pure benzaldehyde. The best results have been obtained by using a mixture of approximately 14 parts air to one part of toluene by weight with the catalyst consisting of a mixture of uranium and molybdenum oxides at a temperature slightly higher than 500° C. and at atmospheric pressure. Time of contact is not mentioned. A still later supplement [98] covers the oxidation of aromatic compounds with more than one side chain. Examples cite the oxidation of o-, m- and p-xylene, pseudocumene, mesitylene and paracymene under conditions which favor aldehyde formation to the exclusion of acids and decomposition products (notably a contact of 0.3 seconds at 550° C.).

Three patents issued in 1924 and 1925 are conspicuous as placing special emphasis upon the preparation of particular catalysts as suitable for reactions involving the partial oxidation of side chains present in aromatic nuclei. The first [99] of these relates to the oxidation of aromatic hydrocarbons and their derivatives, viz., toluene, xylene, cymene, cumene, mesitylene, cresols, etc., together with their derivatives including nitro-

[96] Brit. *Chem. Abstracts* A, 1930, p. 304.
[97] Brit. Pat. 189,091 (1923); U. S. Pat. 1,636,854 (1927) Craver assr. to the Barrett Co.
[98] Brit. Pat. 189,107 (1923) Craver assr. to the Barrett Co.
[99] U. S. Pat. 1,486,781 (1924) Meigs assr. to Carleton Ellis.

compounds, naphthalene, anthracene, and their derivatives, including nitro-compounds. The catalyst consists of an intumesced mass free from inert supporting solids. For example, this may be constructed primarily from two metallic bodies each capable of forming oxides of more than one stage of oxidation such as iron chromate, chromium vanadate, cobalt molybdate, cobalt chromate, nickel vanadate, molybdate or chromate or similar composite catalytic bodies. Such a composite body may be impregnated subsequent to its preparation with single metallic oxides or mixtures of such oxides. For example, an iron molybdo-chromate mass may be impregnated with active vanadium oxide or palladium oxide. Examples which describe in some detail the preparation of certain catalysts corresponding to this general type are given together with an illustration of the general manner in which the oxidation of toluene may be conducted.

The second of these patents [100] deals with the oxidation of toluene, naphthalene and anthracene and refers specifically to the restricted use of certain vanadates of tin and bismuth which have been discovered to possess particular activity in catalyzing oxidation reactions. Examples illustrating the preparation and temperature ranges for different catalysts are given.

The third patent [101] describes a contact mass which may be produced in "most various ways" and which consists of oxides of boron or phosphorus or mixtures of these or their salts (not specified) distributed on carriers of other materials (not specified). The oxidation is effected by using pure oxygen or air or compounds such as the oxides of carbon or nitrogen which are capable of giving off oxygen. An example cites the oxidation of benzyl alcohol to benzaldehyde.

The use of zeolitic types of catalysts has been proposed [102] to overcome some of the difficulties attending the use of single oxide or simple mixtures of oxides as catalysts such as the tendency to form zones of local overheating particularly at the catalyst surface due to too great activity. The zeolitic catalysts consist of base-exchanging polysilicates in which the catalytically active elements may be present in the zeolite nucleus in non-exchangeable form, may be one or more of the exchangeable cations of the zeolite, may constitute an anion to form a salt like body with the zeolite, or may simply be mixed or impregnated in the diluents used with the active zeolites. The nature and proportions of the active materials may be so altered as to make the catalysts applicable to the oxidation of almost any volatile organic compounds with air in the vapor phase. Mixtures of the compounds of such catalytically active metals as vanadium, uranium, tungsten, molybdenum, etc., are applicable in the oxidation of aromatic hydrocarbons to partially oxidized stages. This patent should

[100] Brit. Pat. 228,771 (1925) Maxted and Coke.
[101] U. S. Pat. 1,487,020 (1924) Mittasch, Willfroth and Balz assrs. to the Badische Anilin u. Soda Fabrik.
[102] U. S. Pat. 1,694,122 (1928) Jaeger to the Selden Co.

be consulted for numerous examples, methods of catalyst preparation, and uses. Other methods of preparing complex silicate catalysts have been proposed and uses claimed.[103]

A catalyst formed from iron vanadate and iron oxide supported on asbestos fibers has been proposed for the oxidation of toluene in vapor phase.[104]

Instead of passing the mixed vapors of hydrocarbon and air over a catalyst mass, a method has been proposed in which the catalyst is present in the form of a smoke or aerosol.[105] This condition is obtained by spraying the organic substance containing the catalyst into a heated chamber and mixing with air. For the production of benzaldehyde and benzoic acid from toluene, a colloidal suspension of vanadium oxide in toluene is sprayed so as to be mixed with air in the ratio of 1 to 8, toluene vapor to air, and passed through a chamber at 200° to 300° C. Catalysts similar to those already claimed are mentioned. While this process may have some of the advantages of a homogeneous catalyst, the disadvantages attending the continuous preparation and recovery of catalyst as well as the necessity for spray injection of the hydrocarbon are such as to hinder the successful industrial use of the process.

In order to overcome certain difficulties such as the dissipation of heat and the use of inflammable mixtures, certain liquid phase processes have been proposed for the oxidation of aromatic hydrocarbons and compounds. In such a process [106] the aromatic hydrocarbons or their halogenated derivatives are treated with air or gas containing free molecular oxygen in the liquid phase at temperatures above 150° C. and under pressure in the presence of a substantial quantity of liquid water. A small quantity of such oxidation catalysts as oxides or hydroxides of copper, nickel, cobalt, iron or oxides of manganese, cerium, osmium, uranium, vanadium, chromium and zinc is used. The formation of benzaldehyde from toluene is claimed for the process.

It will have been noted that in the patents which have been referred to particular attention appears to have been directed toward securing conditions favorable to the partial oxidation of side chains present in aromatic compounds. In other words, emphasis must be given to the fact that the desired result of such operations was the production of aldehydes with a minimum accompaniment of acids or of decomposition products. Oxidations in the vapor phase having as their object the preparation of benzoic acids are, with one or two exceptions, conspicuous by their absence in both the general and patent literature. Thus, manufacturing processes analogous to those described in Chapter III and involving the transformation of an alcohol or an aldehyde into the corresponding acid with the intermediate formation of per-acids, have apparently received no attention in

[103] Brit. Pat. 298,142 (1927) Monsanto Chemical Works.
[104] Brit. Pat. 331,525 (1930), 331,535 (1930) Adam, Shannon, and Cockney assrs. to Gas Light and Coke Co.
[105] Caspari, Brit. Pat. 263,201 (1925); U. S. Pat. 1,674,589 (1928).
[106] Brit. Pat. 331,100 (1929); French Pat. 676,826 (1929) I.G. Farbenind.

spite of the fact that it has long been known that benzaldehyde readily lends itself to the type of transformation.[107]

The methods which have been used in the manufacture of benzoic acid have quite generally involved reactions in the liquid phase, viz.: (a) Toluene is chlorinated, heated with milk of lime and finally acidified in order to precipitate the benzoic acid.[108] The product which is obtained in this way is almost always contaminated by the presence of small quantities of chlor-benzoic acid. (b) Benzene is treated with phosgene in the presence of anhydrous aluminum chloride.[109] (c) Toluene is oxidized with a chromic acid mixture in such concentrations of the reacting substances that the product consists of a solution of benzoic acid in toluene.[110] A method by which much of the chlorine-free acid is made consists in the oxidation of toluene by manganous sulfate, potassium permanganate, and sulfuric acid. The necessity for purifying the product obtained in processes involving chlorine and the difficulties attending the purification of such products give the direct oxidation processes a point of superiority.[111] (d) Benzoic acid is also being prepared by the decarboxylation of phthalic anhydride.*

The apparatus employed in toluene oxidation requires a carburetor or vaporizing chamber similar to that employed in naphthalene oxidation in which air is bubbled through the liquid toluene to obtain a high proportion of hydrocarbon in the mixture. Secondary air may be then introduced to dilute the vapor-air mixture to the desired concentration. An alternative method is to spray the toluene into the air stream at the entrance of the reaction chamber or to allow liquid toluene to drip or flow into the chamber at the predetermined rate.

Because of the high vapor pressures of the products obtained in the oxidation, an efficient cooling and collecting system is essential. For this purpose coil condensers followed by scrubbers to remove unreacted toluene and the lighter products have been used. Thiosulfite solutions may be used in scrubbers to remove the benzaldehyde from the reaction mixture and it has been proposed to use activated charcoal scrubbers after the thiosulfite scrubbers to remove unreacted toluene from the non-condensible gases.

The relative proportions in which the products, chiefly benzaldehyde, benzoic acid, and anthraquinone, are obtained depends in a large measure on the temperatures to which the reaction mixture of toluene vapor and air is subjected. High temperatures, together with rapid rates of flow as well as high temperatures and mild catalysts, are conducive to benzaldehyde formation. With vanadium pentoxide catalysts oxidation of

[107] Engler and Wild, *Ber.* 30, 1676 (1897).
[108] U. S. Pat. 1,463,190 (1923) Barstow; *compare also* U. S. Pat. 939,584 (1909); 939,940 and 939,941 (also 1909).
[109] U. S. Pat. 1,542,264 (1925) Norris and Fuller.
[110] U. S. Pat. 1,458,491 (1923) Cooper assr. to McKee.
[111] Phillips and Gibbs, *J. Ind. Eng. Chem.* 12, 277 (1920).
* *Cf.* Chapter XIII.

toluene begins at a temperature of 280° to 300° C., but as the reaction is slow, long times of contact are required and benzoic acid is practically the only product. Not until a temperature of 400° to 450° C. is reached does the speed of reaction become sufficient to enable a 5 per cent conversion of toluene per pass to be realized. Under these conditions, benzaldehyde is the main product amounting to 50 per cent of the toluene reacted. With molybdenum oxide as a catalyst temperatures of 450° to 530° C. are necessary to obtain good yields and benzaldehyde is the primary product.
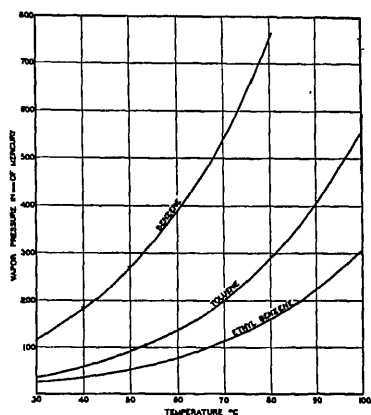
Fig. 36.—Vapor pressure curves for benzene, toluene, and ethyl benzene at low temperatures. (I.C.T.)
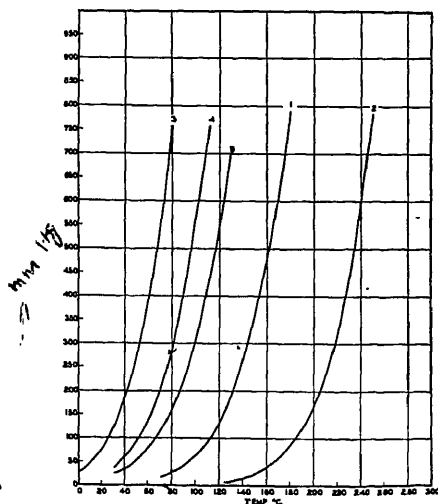
Fig. 37.—Comparison of vapor pressures of:

1. Benzaldehyde   4. Toluene
2. Benzoic acid   5. Ethyl benzene
3. Benzene

Formation of anthraquinone does not occur to more than 5 per cent of the toluene converted and then only within a limited temperature range. The largest amounts are formed at temperatures of 420° to 450° C. over vanadium oxide catalysts.[112] Green also reports the formation of an oil in increasing quantities as the temperature is increased over molybdenum catalysts. At high temperatures (above 500° C.) this oil may account for as much as 20 per cent of the toluene reacted. This oil boiling over a wide temperature range of 280° C. upwards is not formed to any great extent when vanadium catalysts are used.

The reaction to form benzaldehyde and benzoic acid is highly exothermic as shown by the heats of combustion of the reactants.[78]

[112] Green, "Industrial Catalysis," New York, Macmillan Co., 1928, p. 125.

(1) $C_6H_5CH_3(l) + 9O_2 = 7CO_2 + 4H_2O(l) + 934,300$ cal.
(2) $C_6H_5CHO(l) + 8O_2 = 7CO_2 + 3H_2O(l) + 843,100$ cal.
(3) $C_6H_5COOH(l) + 7\frac{1}{2}O_2 = 7CO_2 + 3H_2O(l) + 778,000$ cal.

From (1) and (2)

$C_6H_5CH_3(l) + O_2 = C_6H_5CHO(l) + H_2O(l) + 91,200$ cal.
toluene   *benzaldehyde*

From (1) and (3)

$C_6H_5CH_3(l) + 1\frac{1}{2}O_2 = C_6H_5COOH + H_2O(l) + 156,300$ cal.
toluene   *benzoic acid*

These reaction heats correspond to the evolution of 1545 B.t.u. per pound of benzaldehyde and 2310 B.t.u. per pound of benzoic acid produced. The reaction may best be controlled by the use of low air to toluene ratios, in keeping with the practice in the oxidation of paraffin hydrocarbons and in contrast to the practice in the oxidation of aromatics with two or more nuclei linked together. With mixtures of toluene vapor and the theoretically required air, good conversions of toluene to useful products are obtained when the reaction is restricted to prevent far-reaching oxidation of the entering toluene. Suitable mixtures are obtained by bubbling the air through toluene at a temperature of 60° to 100° C. For good operation the inlet mixture rates should be sufficiently high to maintain a temperature gradient in the catalyst tube reaching a maximum near the exit end of 350° to 450° C. for vanadium catalysts and of 450° to 530° C. for molybdenum catalysts.

The theoretical air required for the oxidation of toluene to benzoic acid, 1.5 mols of oxygen per mol of toluene, amounts to about 30 cu. ft. of air measured at 20° C. (68° F.) and one atmosphere, per pound of toluene oxidized. Similarly, the theoretical air for oxidation to benzaldehyde amounts to 20 cu. ft. per pound of toluene oxidized. The explosive limits of toluene at ordinary pressures and temperatures as measured in narrow tubes or small vessels are: lower limit, 0.003375 lbs. toluene per cu. ft. air (296.5 cu. ft. air per lb. toluene) and upper limit, 0.01927 lbs. toluene per cu. ft. air (52 cu. ft. air per lb. toluene).[113] In the case of the lower aliphatic hydrocarbons as methane and ethane it is well known that the explosive or inflammability limits widen with rise in temperature so that it could well be expected that mixtures of toluene and air leaner than the one given for the lower limit and richer than the one for the upper limit would become inflammable as the temperature becomes higher. The same is true for increase in size of the explosion chamber. Hence, although theoretical mixtures of toluene and air for formation of benzaldehyde and benzoic acid lie on the rich side of the inflammable range,

[113] *Bur. Mines Bull.* No. 279.

such mixtures are difficult to employ because they exert too forceful an oxidizing action on the toluene. The aliphatic side chain of toluene behaves 'like a paraffin hydrocarbon and unless mixtures very dilute in air are used, or mild conditions imposed, will be destroyed completely.

A number of serious difficulties is present in the commercial utilization of the process. In the first place, the possibility of the occurrence of inflammable mixtures of vapor and air introduces a certain hazard from the standpoint of fire and explosion loss. The use of high proportions of air as is done in the case of naphthalene oxidation is not feasible because the oxidation may be carried too far and reduced yields of the desired products obtained. It should be noted, however, that reasonable yields have been obtained with mixtures sufficiently dilute to be beyond the explosive limit.* The use of large proportions of diluents reduces the reaction rate to a point where conversions are prohibitively low. The cooling, collection, and separation of the reaction mixture presents serious problems, especially when diluents are used in the gaseous reaction mixture. The fact that all of the compounds concerned have relatively high vapor pressures makes it necessary for cooling to be sufficient and thorough. Subsequent separation of the products from the dilute toluene solution in which they are collected necessitates several distillations, which are further complicated by the fact that unless recirculation of toluene vapor is employed unreacted toluene must be scrubbed from the waste gases. Recirculation would necessitate intermediate scrubbing of products and enrichment of the reacting mixture with oxygen.

The low value of the raw materials compared to the premium price paid for chloride-free benzaldehyde and benzoic acid makes the commercial utilization of the process attractive despite the difficulties involved. The production of benzoic acid by the direct oxidation of toluene has not reached the proportions that benzaldehyde has. Although the production of benzoic acid directly is feasible with the correct catalysts, small quantities only from this source are being marketed and are obtained as a by-product of the catalytic oxidation of toluene to benzaldehyde. Because of the difficulty in the selection of correct catalysts, the oxidation of toluene to benzoic acid is complicated by the oxidation going too far with resultant loss of raw material or by the formation of gummy condensation products intermixed with the benzaldehyde, benzoic acid, maleic acid and anthraquinone. These complications have deterred commercial application of the oxidation process in the face of the newer process for forming benzoic acid by the decarboxylation of phthalic anhydride.

The production of benzoic acid, U.S.P. in 1928 was 277,202 pounds, as compared with 209,733 pounds in 1927. Benzoate of soda, used chiefly as a food preservative, was manufactured to the extent of 1,027,370 pounds in 1928. The production of benzaldehyde in 1928 was 369,466 pounds.[114]

* Personal communication from Mr. J. M. Weiss.
[114] "Census of Dyes and other Synthetic Chemicals" (1928) U. S. Tariff Commission Information Series No. 38.

Figures are not available to show the relative proportions of these products manufactured by the different processes.

Mechanism of the reaction. As in the case of the oxidation of benzene, accompanied by ring cleavage, the mechanism of the oxidation of alkylated benzene compounds may best be followed by considering the results which have been obtained in the older method of oxidation in the liquid phase.

Aromatic hydrocarbons such as the alkylated benzenes assume an acid reaction when exposed to oxygen over long periods of time,[115] a process which is accelerated by the action of sunlight and ultra-violet light. Ciamician and Silber [116] obtained yields as high as 12 per cent of benzoic acid from toluene by exposing to the action of light for a year. In the same way, the xylenes were found to yield the three toluic acids, and cymene to yield cumic acid. In all cases, monocarboxylic acids were obtained with traces of aldehydes too small to identify. Suida [117] found that some activated oxygen was formed when these hydrocarbons were oxidized to acids in the presence of water vapor and ultra-violet light. Stephens [118] accounts for the presence of this active oxygen by the auto-oxidation of aldehydes, indicating the formation of peroxides and the propagation of chain reactions.

The reactions may also be accelerated by the addition of organic compounds to the hydrocarbon. The oxidation of toluene under the action of light is accelerated by the addition of phenanthraquinone, which is itself attacked in the reaction, however, to form diphenic acid.[119] Anthraquinone and its halogen-substitution products are of greater effect.[120]

The use of inorganic oxides such as those of manganese, cobalt, nickel, and chromium as catalysts in the presence of sulfuric acid for these oxidation reactions resulted in higher yields of products but with only low proportions of aldehydes. For instance, yields of 100 grams of benzoic acid, 8 grams of benzaldehyde, and 100 grams of unreacted toluene are claimed from the treatment of 200 grams of toluene in the presence of manganese oxide and sulfuric acid.[121]

Early claims for the formation of benzaldehyde by liquid phase oxidation are rare. A claim has been made for the oxidation of toluene to benzaldehyde in the presence of sulfuric acid and manganese dioxide at 40° C., however.[122]

It is obvious from a consideration of the temperatures necessary for the oxidation, and from the fact that the alkyl groups attached to an

[115] Weger, *Ber.* **36**, 309 (1903).
[116] *Ber.* **45**, 38 (1912).
[117] *Monatsh.* **33**, 1255 (1912).
[118] Stephens, *J. Am. Chem. Soc.* **48**, 1824-6 (1926).
[119] Benrath and Meyer, *Ber.* **45**, 2707 (1912).
[120] Eckert, Brit. Pat. 182,487 (1923).
[121] a. Senderens, U. S. Pat. 1,365,956 (1921). *See also* b. Shorigin, Kizberg, Troitzkii, and Smolyaninova, *J. Chem. Ind. (Moscow)* **6**, 258-60 (1929); c. Kakutani and Yamagughi, *Repts. Imp. Ind. Research Inst. (Osaka)* **9**, No. 11, 1929 (*Chem. Abstracts* **23**, 3217 (1929)); d. King, Swann, and Keyes, *Ind. Eng. Chem.* **21**, 1227-31 (1929).
[122] Monnet, U. S. Pat. 613,460 (1898).

aromatic nucleus are the first points of attack that the aromatic hydrocarbons are more difficult to oxidize than the paraffins. It has been found that normal paraffin hydrocarbons containing from five to seven carbon atoms and cyclohexane are oxidized from 700 to 2000 times faster than benzene.[128] The same workers also showed that aromatic hydrocarbons with side chains are oxidized from 1000 to 6000 times faster than benzene. Whether or not the values for these rate ratios are representative, the fact remains that the side chains are the first points of attack by the oxygen. This fact makes it easily possible to obtain high conversions of the hydrocarbons into oxygenated products as acids and aldehydes together with high yields and at relatively high rates.

The presence of alcohols has not been reported in the oxidation of these hydrocarbons, and although this fact does not preclude the intermediate formation of an alcohol as the first step in the oxidation, it does indicate that the mechanism of side chain oxidation is similar to that of aliphatic hydrocarbon oxidation since in this latter case even the proponents of the hydroxylation theory have had difficulty in isolating alcohols.

As in the case of liquid phase oxidation the lowest oxidation product to have been isolated from toluene in vapor phase processes is benzaldehyde, which is obtained so regularly and in such quantities in the various experiments that have been performed with a great variety of catalysts, that it would seem as though the mechanism did not require atomic oxygen but occurred through the formation of a dihydroxy derivative which instantly decomposed. Thus:

$$\text{C}_6\text{H}_5\text{CH}_3 + \text{O}_2 \longrightarrow \left[\text{C}_6\text{H}_5\text{CH}{<}^{\text{OH}}_{\text{OH}} \right] \longrightarrow \text{C}_6\text{H}_5\text{CHO} + \text{H}_2\text{O}$$
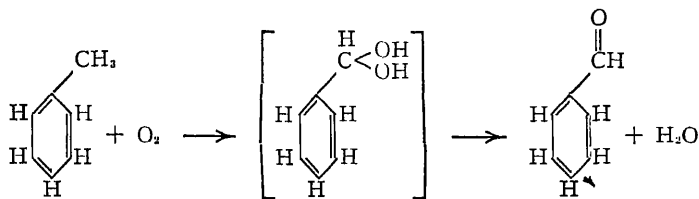
If benzyl alcohol were formed as the first step, it should be possible to isolate it in the early stages of the oxidation, and yet its formation has not been reported.

Although the oxidation affects only the alkyl group attached to the benzene nucleus, the presence of more than one methyl group accelerates the oxidation. Thus, in the liquid phase non-catalytic oxidation experiments of Stephens it was found that durene (sym.-tetra methylbenzene) was easily oxidized under conditions that scarcely affected toluene. However, in the presence of water the oxidation of m-xylene or mesitylene (1:3:4-trimethylbenzene) is almost entirely inhibited,[128] a fact that Stephens interprets as showing the reversible elimination of water in one

[128] Tronov, Popov, Kolotovkin, and Stalash, *J. Russ. Phys. Chem. Soc.* **61**, 2390 (1929).

of the steps of the process, and which supports the mechanism given above. Dimethyl benzene (o-xylene) is easily oxidized, however, to phthalic anhydride in the vapor phase in the presence of a tin vanadate catalyst [124] at temperatures of 270° to 310° C. A 59.4 per cent yield of anhydride was obtained at 290° C.

The subsequent oxidation of benzaldehyde to benzoic acid is much more critical and requires a directive catalyst. The reaction involves the addition of a single atom of oxygen to the molecule. The fact that with certain catalysts at temperatures of 500° C. yields of oxidized organic compounds consisting almost exclusively of benzaldehyde may be obtained even in the presence of large excess of air is difficult to explain, especially since benzaldehyde is ordinarily looked upon as an easily oxidized compound. The relative proportions of aldehyde and acid formed in the process depends upon the relative rates of the two reactions:

$$RCH_3 + O_2 = RCHO + H_2O$$
$$2RCHO + O_2 = 2RCOOH.$$
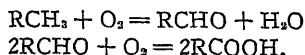
At the start of the reaction the higher concentration of the hydrocarbon favors the first reaction, but as the reaction proceeds or as the temperature becomes higher the second reaction proceeds at a rapid rate as evidenced by the high ratios of acid to aldehyde that have been reported in catalyzed reactions. However, by oxidizing in the liquid phase in the absence of light at 100° C. without catalysts, aldehyde may be obtained as the main product with acid as a minor and secondary product.[118] This somewhat surprising result in the light of the previously reported data apparently indicates that the second step in the oxidation proceeds at a slower rate than the first in the absence of active catalysts or sources of energy as light. This is due to the fact that the oxidation of benzaldehyde to benzoic acid involves only one atom of oxygen. The reaction as written above for molecular oxygen is trimolecular, sufficient evidence to say that it does not occur in this way.

When benzaldehyde is allowed to stand in an atmosphere of oxygen, the rate of oxidation is determined by the rate at which oxygen diffuses to the active wall surface.[125] Complete removal of water vapor results in practically zero oxidation. Very pure benzaldehyde does not show any autoxidation in air. The abnormal fall in the slope of the oxidation curve as oxidation proceeds in the presence of water vapor is probably due to the poisoning of the active wall surface by the adsorption of oxidation or condensation products such as water. Under certain conditions, such as absence of light and water vapor, benzaldehyde forms a peroxide that is capable of oxidizing a potassium iodide solution. Exposure to light, however, destroys the peroxide.[126]

This oxidation of benzaldehyde is subject to acceleration by the action

[124] Maxted, *J. Soc. Chem. Ind.* 47, 101-5T (1928).
[125] Reiff, *J. Am. Chem. Soc.* 48, 2893-9 (1926).
[126] Jorissen and van der Beck, *Rec. trav. chim.* 49, 138-41 (1930); *see also ibid.* 46, 42-6 (1927).

of catalysts. Small additions of iron, copper, nickel or manganese salts accelerate the oxidation of very pure benzaldehyde considerably.[127] One mol of ferric chloride in 1200 mols of benzaldehyde is sufficient to cause the oxidation of half the aldehyde in 40 minutes in presence of air at 20° C. The ferrous salts are about fifteen times more active than the ferric for this reaction. Substances such as hydrocyanic acid and phosphoric acid act as poisons and inhibit the reaction. This catalytic action of certain salts in a way explains the presence of such small amounts of benzaldehyde as were found in the oxidation of toluene in the presence of sulfuric acid and manganese dioxide, since under the conditions of the experiments the benzaldehyde must have had a higher rate of oxidation than the toluene after a certain concentration had been reached.

In the vapor phase oxidation of toluene it has been found that the relative proportions of the different products may be varied by the proper choice of catalysts. In general, the oxides of molybdenum, tungsten, zirconium, and tantalum promote oxidation to the aldehyde but are not sufficiently active to promote the further oxidation to any great extent. Oxides of manganese, copper, nickel, chromium, uranium, are more powerful in their action and although they favor the formation of aldehyde, they also promote the complete combustion of the hydrocarbon. Cobalt and cerium favor complete combustion. The oxides of titanium, bismuth, and tin are not active and require such high temperature for the initiation of reaction that more profound changes occur resulting in high losses of raw material. Vanadium oxide is particularly active in promoting the oxidation of benzaldehyde to benzoic acid, so that high conversions to acid may be obtained by its use.

In the oxidation of toluene to benzoic acid in the vapor phase catalytic process the step in the process involving the oxidation of benzaldehyde controls the rate at which benzoic acid is formed at a given temperature. This is illustrated in the results obtained with a tin vanadate catalyst.[124] In these experiments the tin vanadate catalyst did not develop activity for the oxidation of benzaldehyde until a temperature approximately equal to that necessary for the oxidation of toluene to benzoic acid was reached. Also, the maximum yield of benzoic acid from benzaldehyde was not greater than that from toluene, being controlled probably by the stability of the benzoic acid formed under the circumstances. The space-time yields in the two instances are of the same order of magnitude. The metallic oxide catalysts are specific in their action in this step of the oxidation and catalysts that favor oxidation of benzaldehyde to benzoic acid will be the most suitable for the oxidation of toluene to benzoic acid. Catalysts which give high rates of conversion of benzaldehyde to benzoic acid are sufficiently powerful to cause further combustion with the result that although the rate at which acid may be formed is high, the conversion of

[127] Kuhn and Meyer, *Naturwissenschaften* 16, 1028-9 (1928).

aldehyde or hydrocarbon to acid is reduced. This is true of cerium oxide and cobalt oxide.

The further oxidation of benzaldehyde to benzoic acid is complicated also by the numerous condensations and polymerizations that occur. At 350° C. benzaldehyde decomposes to benzyl benzoate with the formation of some benzene and carbon monoxide.[128] At the same temperature benzyl benzoate decomposes to benzoic anhydride, toluene, and benzaldehyde. At temperatures of 700° C. carbon monoxide and benzene are the chief decomposition products of benzaldehyde and some diphenyl and triphenyl also form. In the presence of catalysts and oxygen further reactions lead to the formation of complicated gums and tars which involve losses, make separation of the product difficult and effectively destroy the activity of the catalyst by coating it over.

With a vanadium pentoxide catalyst supported on aluminum at temperatures of about 400° to 500° C. and air-toluene vapor volume ratios of about 7.5 to 1, small amounts of anthraquinone have also been obtained in the oxidation of toluene to benzaldehyde and benzoic acid.[129] Thus Bowen and Nash,[129] using an apparatus similar to that of Downs,[129] oxidized toluene under the following conditions: temperature of toluene in saturator, 50° C. (V.P. 93.53 mm. mercury); vanadium pentoxide on aluminum catalyst; reactor temperature 400° C.; and obtained as a product: 0.30 grams of yellow needle crystals (anthraquinone); 4.87 grams of white flake crystals (benzoic acid); 0.37 grams of a mixture of these two substances; 7.3 cc. of water; 6.5 cc. of unreacted toluene; and 24.7 cc. of an oily condensate, 18 cc. of which gave 16 cc. distilling off up to 115° C. and left about 2 cc. of crude benzaldehyde. This formation of anthraquinone has been accounted for by Downs on the basis of the oxidation and condensation of benzaldehyde as follows:

benzaldehyde   *anthraquinone*
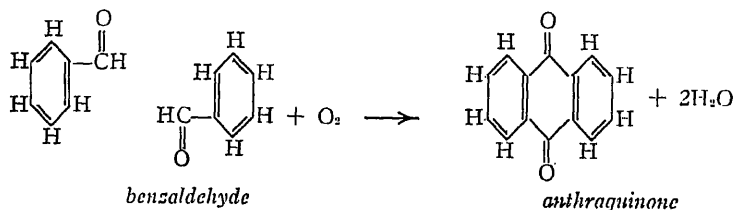
It is, of course, possible to devise other condensation reactions to account for the anthraquinone formation. Sufficient data have not been published to make possible an evaluation of the significance of this reaction.

When the benzene nucleus contains an alkyl group with a longer chain than the methyl group of toluene, oxidation occurs more readily, as is true also of the paraffin hydrocarbons where ethane is more readily oxidized

[128] Hurd and Bennett, *J. Am. Chem. Soc.* **51**, 1197 (1929).
[129] a. Downs, *J. Soc. Chem. Ind.* **46**, 383T (1927); b. Bowen and Nash, *Nature* **120**, 621 (1927); *J. Inst. Pet. Tech.* **14**, 106-14 (1928).

than methane. This is shown by data on ethyl benzene oxidation where a tin vanadate catalyst was used.[124] Yields of benzoic acid in the form of a pure crystalline sublimate were obtained on the condenser walls of the apparatus as in the case of toluene oxidation.

TABLE XXXVII.—*Ethyl Benzene Oxidation.*

(Experiments made with a carburetor temperature of 65° C. A primary air space velocity of 200 and a secondary air space velocity of 600.)

Catalyst Temperature	Yield Benzoic Acid Per Cent	Space Time Yields
260° C.	18.0	0.0098
270	39.4	0.0214
280	41.3	0.0224
285	37.7	0.0205
290	22.4	0.0122

$$\text{Space velocity} = \frac{\text{liters of gas at standard conditions}}{\text{(hour) (liter of catalyst space)}}$$

These results are to be compared with those for toluene in which the same tin vanadate catalyst was used at a temperature of 290° C. Benzoic acid was the only product condensed.

TABLE XXXVIII.—*Oxidation of Toluene.*

(Toluene carburetor temperature 40° C.)

Space Vel. Primary Air	Space Vel. Secondary Air	Vols. Air* per Vol. Toluene Vapor	Yield Benzoic Acid Per Cent	Space† Time Yields of Acid
200	500	40.8	53.3	0.020
200	700	52.5	41.0	0.0112
200	1000	70.0	36.3	0.0135
300	2000	88.6	32.9	0.0137
300	3000	128.6	23.8	0.0105

* Calculated on basis of saturation of air by toluene vapor in carburetor.

† Space time yield $= \dfrac{\text{grams of product}}{\text{(hour) (cc. of catalyst space)}}$

The experiments were conducted in an apparatus similar to that shown in Figure 38. The primary air is passed through a carburetor containing the material to be oxidized and maintained at a suitable temperature for vaporization, is joined at the reactor by a stream of secondary air, and is then passed through a 9 mm. inside diameter quartz U tube containing 10 cc. of catalyst and immersed in a bath of a eutectic mixture of potassium and sodium nitrates. Figure 39 shows the results with a number of substances in graphical form. It is to be noted that rather high ratios of air to toluene vapor were used in the experiments and that all yields are based on a once through basis, i.e., unreacted material is considered lost.

In the case of the liquid phase non-catalytic oxidation of ethyl benzene and n-propyl benzene the oxygen behaves in the same manner as the
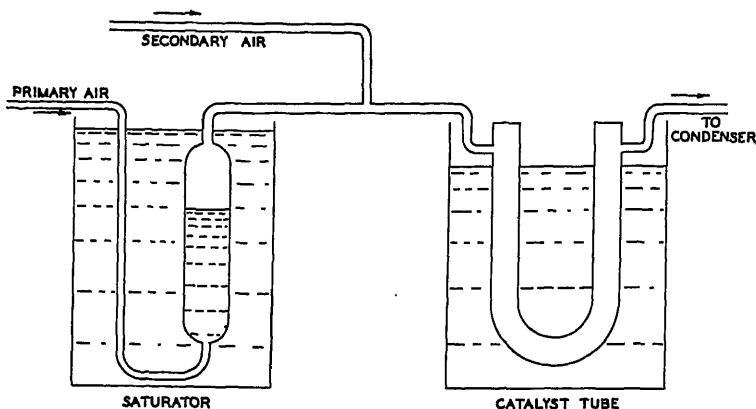
FIG. 38.—Apparatus for laboratory scale oxidation of benzene and toluene.

halogen.[180] The hydrogen attached to the carbon atom nearest to the ring is removed and acetophenone and propiophenone respectively are obtained. The use of inorganic catalysts to accelerate the rate of the liquid phase oxidation does not alter the mechanism of the oxidation since acetophenone is still obtained from ethyl benzene in good yield.[121d] Using 2 per cent of manganese acetate in the ethyl benzene and oxidizing with oxygen at 102° to 104° C., King, Swann and Keyes were able to obtain a yield of 20.6 per cent acetophenone in 24 hours, compared to a yield under similar conditions without a catalyst of only 1.67 per cent in the first 24 hours. Metallic oxide catalysts, however, were of little benefit, cerium oxide being the best of those tried. With cumene and p-cymene the isopropyl group lost one methyl group and the hydrogen attached to the alpha carbon atom and a ketone formed. Some oxidation of the methyl group occurred with cumene resulting in the formation of some cumic aldehyde

FIG. 39.—Results of Maxted [124] on oxidation of a number of different substances.

Curve	Substance	Temp. Carbu- retor ° C.	Space Velocity of Air Pri- mary	Secon- dary
1	o-Xylene	70	200	600
2	Benzaldehyde ..	100	1000	none
3	Ethyl benzene ..	65	200	600
4	Benzyl alcohol..	145	600	600

[180] Stephens, *J. Am. Chem. Soc.* 48, 2920-2 (1926).

and cumic acid. Formic acid was obtained by oxidizing cumene at 80° C. showing that the methyl group which was lost by the nucleus was oxidized to formic acid and at higher temperatures to water and carbon dioxide. With tert-butyl benzene no appreciable oxidation occurred at 102° to 104° C. in 25 days. Apparently, for this type of oxidation it is essential that the alpha carbon of the attached chain have a hydrogen atom directly attached.

Oxidation of other benzene derivatives. Aromatic hydrocarbons which contain in addition to a methyl group, a halogen atom or nitro group attached to the nucleus, may be oxidized in the side chain to carboxylic aromatic acids without splitting off the halogen or nitro groups as in the wet method.[131] Fair yields of the corresponding acid are obtained in the presence of a granular tin vanadate catalyst. With an air rate of 10 liters per hour and passing 0.3 grams of p-nitrotoluene over the 10 cc. of catalyst per hour an 8.4 per cent yield of p-nitrobenzoic acid was obtained at 260° C. and a 14 to 16 per cent yield at 270° to 300° C. Little or no acid could be obtained from o-nitrotoluene as the product decomposed at the catalyst temperatures necessary to use for the oxidation. With o-bromo- and o-chlorotoluene yields of the corresponding acids were obtained as shown below.

o-Bromotoluene

Temp. ° C.	255	265	275	285	290	295	305
Yield of acid (per cent)	7.4	12.1	13.7	21	24.3	14	6.3

o-Chlorotoluene

Temp. ° C.	260	275	285	287	293
Yield of acid (per cent)	4.9	7.4	21.3	13.8	12.6

Although little experimental data is available, numerous patents have been issued for the vapor phase catalytic oxidation of various other derivatives containing the benzene nucleus, as well as heterocyclic compounds. Thus, fluorene (diphenyl methane) is oxidized to fluorenone with air in the presence of a catalyst containing iron vanadate or other suitable metal salt of the fifth or sixth group of the periodic system at a temperature of 360° to 400°.[132] Maleic acid and anhydride are formed by the catalytic oxidation of compounds of the furan series, such as furan, furfural alcohol, furfural, methyl furfural, hydroxymethylfurfural, pyromucic acid or mixtures, with air over catalysts of molybdenum, vanadium, or other metals.[133] Dimethyl benzaldehyde is formed by oxidizing pseudocumene with air at 550° C. in the presence of a tungsten oxide catalyst. Molybdenum, vanadium, or tantalum oxide catalysts may also be used to form aromatic aldehydes from o-, m-, or p-xylenes, mesitylene, p-cymene, or o-chlorotoluene by air oxidation. Times of contact of 0.3 to 0.4 seconds

[131] Maxted and Dunsby, *J. Chem. Soc.* 1928, 1439-42.
[132] U. S. Pat. 1,764,023 (1930) Jaeger to the Selden Co.
[133] a. Brit. Pat. 285,426 (1927) Boehringer; b. Ger. Pat. 478,726 (1927) Boehringer Sohn; *see also* c. Brit. Pat. 253,877 (1925) Yabuta, anodic oxidation; d. Killefer, *Ind. Eng. Chem.* 18, 1217-9 (1926).

are specified and ratios of air to hydrocarbon of about 8.3 are used.[184] It has been claimed that under proper conditions o-cresol may be oxidized to salicyl aldehyde or salicylic acid. Catalysts as iron or aluminum oxides, or oxides of the metals of the fifth and sixth groups of the periodic system, especially molybdenum oxide, are claimed. By operating at a temperature of 250° to 500° C. in the presence of diluent gases such as carbon dioxide complete combustion is prevented.[185] No operating details are given, no data presented in the patent, and the conditions described in such general terms as to leave the possibility of such reaction in doubt.

Ortho-cresol in benzene solution absorbs oxygen at a much higher rate than phenol under similar conditions, however, and it is possible that similar relations will hold in the vapor phase. Although no data in regard to the type of products formed in this liquid phase oxidation are reported, the great difference in absorption rates is noteworthy. One-half gram molecular weight of phenol and o-cresol dissolved in 100 cc. of benzene and exposed to oxygen in the presence of 609.5 sq. cm. of copper surface gave the following results:

| | Rate of Oxygen Absorption cc./day | |
Day	Phenol	o-Cresol
1	4	12
2	7	36
3	10	108
4	12	139
5	15	155
Total cc. O_2 in 5 days	48	450

A greenish crystalline compound containing about 45 per cent copper was found in the product and probably acted as a catalyst for the oxidation.[186]

In 1923 patents [187] were granted for a process relating to the manufacture of benzaldehyde or benzoic acid by the oxidation of dibenzyl. The claims made in these patents are based on the discovery that the above reaction takes place without the intervention of any oxygen carrier or catalyst, simply by bringing molecular oxygen (pure or mixed with inert diluent gases) into contact with dibenzyl at temperatures of about 150° to 284° C. (the latter representing the boiling point of dibenzyl) under atmospheric pressure or 150° to 500° C. (preferably 200° to 300° C.) under higher pressures. The process is designed for continuous operation and the claim is made that it may be so controlled as to give quantitative yields. The industrial significance of such a process, no matter if it is non-catalytic in character, will depend upon the availability of dibenzyl as a by-product or upon methods of manufacture which are cheaper rela-

[184] U. S. Pat. 1,636,855 (1927) Craver.
[185] U. S. Pat. 1,380,277 (1921) Weiss and Downs to the Barrett Co.
[186] Skirrow, *Can. Chem. J.* 3, 292-4 (1919).
[187] Brit. Pat. 197,319 (1923) Curme, assr. to Union Carbide and Carbon Chem. Co.; U. S. Pat. 1,463,255 (1923) Curme and Heyn assrs. to Union Carbide and Carbon Chem. Co.

tively than the difference in cost of operating a catalytic toluene oxidation process and a non-catalytic dibenzyl oxidation process.

Recently Senseman and Stubbs [138] have studied the catalytic, vapor phase oxidation of p-cymene. Previous work on the liquid phase oxidation of this substance had shown it to be readily acted upon by potassium permanganate, nitric acid, or chromic acid. The catalytic vapor phase oxidation led to the formation of water, carbon dioxide, formaldehyde, formic acid, p-toluic acid, and terephthalic acid. The product obtained in greatest yield was p-toluic acid, showing that the primary point of attack of the oxygen was the isopropyl substituent. Thus:

$$CH_3 \cdot C_6H_4 \cdot CH(CH_3)_2 + 4\tfrac{1}{2}O_2 = CH_3 \cdot C_6H_4 \cdot COOH + 2CO_2 + 3H_2O.$$
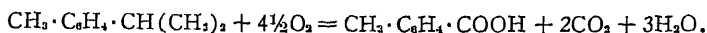
It was found, however, that from three to six times the calculated amount of air (approx. 4.6 liters air per gram cymene) was necessary to obtain the highest yields of acid. Smaller amounts of air led to the formation of a preponderance of aldehydes, particularly when low catalyst temperatures were used. A catalyst formed by depositing vanadium pentoxide on broken porcelain from an ammonium metavanadate solution by evaporation and heating was found to be generally superior to a fused vanadium pentoxide catalyst. Both forms of the vanadium catalysts were superior to tin vanadate or manganese dioxide. A maximum yield of 16.9 per cent of p-toluic acid was obtained at 375° C., a space velocity of 300, and a cymene to air ratio of 0.052 grams per liter. Under these conditions a yield of water soluble acid of 7.7 per cent (calculated as formic) was obtained. Space time yield of p-toluic acid was 0.0026 and increased to 0.0032 as the space velocity was raised to 375, although the yield of acid dropped at the same time to 15.9 per cent.

[138] Senseman and Stubbs, *Ind. Eng. Chem.* **23**, 1129-31 (1931).

Chapter XIII

Oxidation of Naphthalene

Source of Naphthalene

Crude coal-tar, the source of raw materials used in the synthesis of aromatic chemicals, is obtained largely in the manufacture of by-product coke, more than 95 per cent of all the coal-tar produced in the United States being obtained from by-product coke oven operation. In 1928, the combined output of coke-oven and coal-gas tar was 688,344,767 gallons, an increase of 14.5 per cent over 1927.[1a] During 1930 the production of coal-tar dropped to 647,485,929 gallons reflecting the general depression of industry.[1b] Over half of this production is used as a fuel largely in metallurgical processes, and a considerable portion is distilled into a number of products having wide commercial uses, among them being the manufacture of organic dye intermediates.

Distillation of the crude tar yields two groups of products: (1) Complex mixtures resulting from fractional distillation and being sold under the names of solvent naphtha, light oil, dead oil, creosote oil, and anthracene oil; (2) coal-tar crudes such as benzene, toluene, naphthalene, anthracene, and the less important cumene, carbazole, cresols, and pyridine. Coal-tar intermediates are prepared by purification of these crude products and are used in the manufacture of dyes and other products.

The composition of a mixture of four representative coke-oven tars with a specific gravity at 15.5° C. of 1.186 and a benzene insoluble of 10.6 per cent is shown in Table XXXIX, as determined by Weiss and Downs.[2] The amounts given should not be taken as commercially recoverable, since practical methods of refining would not permit the isolation of all of any one constituent in the tar.

Naphthalene occurs in coal-tar to the extent of about 10 per cent and is contained in the middle fraction (180° to 250° C.) of the distillate from the tar. The output of refined naphthalene in 1930 was 31,955,635 pounds, in 1929 it was 31,143,716 pounds, in 1928 24,992,092 pounds, and in 1927 only 21,233,131 pounds.[1a, b]

By redistillation of the middle fraction a product containing over 45 per cent naphthalene is obtained. The naphthalene is allowed to crystallize slowly over a period of about 10 days to form large crystals, and the oil

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[1] a. Census of Dyes (1928), U. S. Tariff Com., Information Series **No. 38**, p. 13; b. *ibid.* (1930), Second Series **No. 19**, p. 4.
[2] Weiss and Downs, *Ind. Eng. Chem.* **15**, 1022-3 (1923).

TABLE XXXIX.—*Composition of Coal Tar.*

	Per Cent by Weight on Dry Tar
Light oil:	
Crude benzene and toluene	0.3
Coumaron, indene, etc.	0.6
Xylenes, cumenes, and isomers	1.1
Middle and heavy oils:	
Naphthalene	10.9
Unidentified in naphthalene and methyl naphthalene range	1.7
Alpha monomethyl naphthalene	1.0
Beta monomethyl naphthalene	1.5
Dimethyl naphthalenes	3.4
Acenaphthene	1.4
Unidentified in acenaphthene range	1.0
Fluorene	1.6
Unidentified in fluorene range	1.2
Anthracene oil:	
Phenanthrene	4.0
Anthracene	1.1
Carbazole and allied nonbasic nitrogen compounds	2.3
Unidentified oils, anthracene range	5.4
Phenol	0.7
Phenol homologs (cresols and xylenols)	1.5
Tar bases (pyridine, picolines, lutidenes, quinolines, and acridine)	2.3
Yellow solids of pitch oils	0.6
Pitch greases	6.4
Resinous bodies	5.3
Pitch (460° F. melting point)	44.7
	100.0

separated by centrifuging or "whizzing." The crude naphthalene thus obtained distills about 57 per cent by volume over at 215° C. and 93 per cent over at 220° C., and has a melting point of 65° to 75° C. This material obtained in the first centrifuging is purified either by (1) hot pressing in hydraulic presses, or (2) remelting, crystallizing, centrifuging, and washing with hot water in the centrifuge. The same result that is accomplished in method (2) is obtained by a patented process which involves the slow crystallization of naphthalene while undergoing agitation with hot water, cooling while agitation is continued, and finally centrifuging. This "hot pressed" or "purified" product melts at 77° to 78.5° C., and is suitable for use in oxidation to phthalic anhydride. The impurities present in this product are not poisons for the catalysts used in the oxidation and burn during the oxidation so that they do not contaminate the product.

If the naphthalene is to be used in processes involving hydrogenation over nickel catalysts the "hot pressed" or "purified" naphthalene is subjected to further treatment. Treatment with sulfuric acid followed by washing removes some of the impurities that are still present. A subsequent caustic soda treat followed by vacuum or steam distillation results in the production of refined naphthalene with a melting point of 79° to 79.8° C. (melting point of pure naphthalene 80° C.). For the removal of

catalyst poisons which may still remain various patented processes have been developed,[3] such as treatment with an easily melted alkali metal as sodium,[3a] heating under pressure with caustic alkali, at 280° C.,[3b] heating at 100° C. with 7 per cent of the chloride of sulfochloracetic acid,[3c] etc. Aromatic hydrocarbons in the relatively crude state may be purified of such impurities as acyclic, and heterocyclic compounds, organic or inorganic sulfur compounds, or phenols by a process of differential halogenation to convert impurities into readily separable or harmless substances. Gaseous or liquid chlorine or substances yielding chlorine may be used.[4] Catalysts, ultra-violet light, heat, pressure, or silent electric discharge facilitate the treatment.

Oxidation of Naphthalene

The vapor phase catalytic oxidation of naphthalene results in the formation of naphthaquinone, phthalic anhydride, phthalic acid, maleic anhydride, benzoic acid, carbon dioxide, water, etc. Commercially, phthalic anhydride is the most important of these products and the oxidations are so conducted as to yield the largest possible quantity of the substance in as pure a condition as possible.

Phthalic anhydride is the raw material for anthraquinone used in the manufacture of many vat dyes and in alizarin and alizarin derivatives. It is used directly for the fluorescein, eosine, and rhodamine dyes. Several esters are made from the anhydride and are largely used in the lacquer industry as plasticizers. Combined with glycerin, phthalic anhydride forms the glyptal and rezyl resins which are giving promise of increased commercial application. Other outlets are in the manufacture of phenolphthalein and in the recently perfected methods for production of chloride-free benzoic acid. It is interesting to note that phthalic anhydride has outlived the use for which it was originally produced, i.e., synthetic indigo manufacture. The availability of so cheap and reactive an organic intermediate as phthalic anhydride should lead to further expansion in its use, and the increased production thus induced should still further decrease the costs.

Production of phthalic anhydride by the catalytic oxidation of naphthalene in 1928 was the highest on record—6,030,854 pounds.[1a] In 1929 this production rose to 9,168,946 pounds and in 1930 dropped 27 per cent to 6,693,001 pounds.[1b] The price of phthalic anhydride has dropped steadily from $4.23 per pound in 1917 to 20 cents in 1925, and to 16.3 cents in 1928. The price in 1930 was quoted as 18 cents in barrel lots.

Phthalic anhydride was discovered at least as early as 1836 by Laurent,[5]

[3] a. U. S. Pat. 1,763,410 (1929) Schroeter assr. to Newport Mfg. Co.; b. Ger. Pat. 483,759 (1927) Ges. f. Teerverwertung; c. French Pat. 602,408 (1924) Comp. de Prod. Chim. et Elec. Alais, Froges et Camargue.
[4] U. S. Pat. 1,741,305-6-7-8-9-10 (1926) Jaeger assr. to Selden Co.; b. Brit. Pat. 290,840, 299,419 (1927) Selden Co.; c. French Pat. 636,485 (1927) Selden Co.; d. French Pat. 662,828 (1928) Selden Co.; e. U. S. Pat. 1,729,543 (1929) Jaeger assr. to Selden Co.
[5] Laurent, *Rev. sci.* 14, 560; *Compt. rend.* 21, 36; *Ann.* 19, 38 (1836).

who prepared the acid by the oxidation of naphthalene with chromic acid and obtained phthalic anhydride by the sublimation of the acid.[6]

Although capable of synthesis by other methods, phthalic acid and anhydride have always been prepared on a commercial scale by the oxidation of naphthalene. The early methods involved liquid phase processes in which expensive nitric and chromic acid were used for the oxidizing agents.[7] During the latter part of the nineteenth century, however, the growing demand for the acid as an intermediate for dye manufacture made it imperative that cheaper means for its production be found. As a result of research by the larger chemical concerns a method of oxidizing naphthalene by sulfuric aid in the presence of mercury salts to form phthalic anhydride was perfected and patented by the Badische Anilin u. Soda Fabrik in 1896.[8] The method was employed on an enormous scale by this company in its development of the synthetic indigo dyes.[9] Improvements of the original sulfuric acid process have been proposed from time to time but none have any great advantage.

Numerous other liquid phase processes have been invented but without supplanting the sulfuric acid method. Thus, naphthalene is oxidized to phthalic acid by potassium permanganate in boiling water.[10] Naphthols and other naphthalene derivatives are oxidized to phthalic acid by heating an alkaline solution with various metallic oxides and peroxides.[11] In place of the mercury salts first used in sulfuric acid oxidation compounds of the rare earths have been proposed.[12] Electrolytic oxidation of naphthalene to naphthoquinone, or phthalic acid in an acid solution in the presence of cerium salts as catalysts has been tried.[13] Oxidations are conducted in the presence of alkalies for the purpose of neutralizing the acids as rapidly as they form.[14] Alkali chlorate solutions activated with osmium tetroxide are powerful oxidizing agents [15] useful in the oxidation of hydrocarbons of the benzene and naphthalene series. Copper, iron, or nickel oxides or hydroxides are active as catalysts in the liquid phase oxidation of aromatic compounds with oxygen [16] and in the presence of substantial amounts of liquid water.

When the supply of phthalic anhydride from Germany was cut off by the war, the manufacture of the compound was undertaken in this country. Attempts to use the old sulfuric acid liquid phase process on the basis of patent disclosures showed the unsatisfactory nature of the method. The

[6] *See also* Gibbs, *Ind. Eng. Chem.* **12**, 1017 (1920).
[7] Lüddens, *Chem. Ztg.* **15**, 585 (1891); *J. Soc. Chem. Ind.* **10**, 758 (1891).
[8] Ger. Pat. 91,202 (1896); Brit. Pat. 18,221 (1896) Badische Anilin und Soda-Fabrik.; *cf.* *Chem. Zentr.* **68**, 1040, I (1897); *J. Soc. Chem. Ind.* **16**, 676 (1897).
[9] Conover and Gibbs, *Ind. Eng. Chem.* **14**, 120 (1922).
[10] Prochazka, *Ber.* **30**, 3108 (1897).
[11] Imray, Brit. Pat. 15,527 (1901); *also* Ger. Pat. 138,790 (1903), 139,956 (1903), 140,999 (1903); *see also* Ger. Pat. 136,410 (1902); *J. Chem. Soc.* **84A**, 487,561 (1903); *J. Soc. Chem. Ind.* **20**, 1139 (1901); *Chem. Zentr.* **73** (II), 1371 (1902), **74** (II), 1106 (1903).
[12] Ditz, Ger. Pat. 158.609 (1905); *Chem. Ztg.* **29**, 581-2 (1905); *J. Chem. Soc.* **88A**, 516 (1905); *Chem. Zentr.* **76** (I), 841 (1905).
[13] Ger. Pat. 152,063 (1904).
[14] Charitschkoff, *Chem. Ztg.* **33**, 1165 (1909).
[15] Hofmann, Ehrhart and Schneider, *Ber.* **46**, 1657-68 (1913).
[16] Brit. Pats. 318,550 (1928); 331,100 (1929) I.G. Farbenind.

yields obtainable varied from 55 per cent of theoretical to an average of 25 per cent of theoretical. The discovery of the effectiveness of the oxides of the metals of the fifth and sixth groups of the periodic system, especially of vanadium and molybdenum oxides, in the vapor phase oxidation of toluene to benzaldehyde and benzoic acid by air led to the use of similar catalysts in a similar process for the production of phthalic anhydride from naphthalene.[17] On June 16, 1917, the U. S. Department of Agriculture announced that the Color Laboratory of the Bureau of Chemistry had developed a laboratory scale process for this vapor phase, catalytic oxidation of naphthalene, and was ready to cooperate with manufacturers in developing the process on a commercial scale. Although a number of companies cooperated at the time, a large number of patents were issued, and the process was developed to a commercial scale, very little information has been disclosed in the general literature regarding details.

By the original process [18] naphthalene is melted and caused to flow continuously at a measured rate into a heated chamber where it is volatilized. This vapor of naphthalene is then mixed with air in excess of the proportion theoretically required to oxidize naphthalene to phthalic anhydride, four times the theoretical amount being preferable. The mixture of air and naphthalene vapor is passed into a reaction chamber maintained at a temperature ranging from 350° to 550° C., the preferred temperature being 500° C. In this chamber the gas mixture is forced in close contact with oxides of molybdenum in the form of a fine powder supported on trays, where by means of baffle plates the current of mixed gases is forced through it. Pressure sufficient only to cause the gases to flow continuously is used. The products of reaction consist of phthalic anhydride and other oxidation products of naphthalene as naphthoquinone, benzoic acid, etc., and are condensed together with unreacted naphthalene by cooling. Phthalic anhydride is subsequently recovered from the other constituents of the mixture by fractional sublimation. Oxides of vanadium alone or mixed with other substances such as magnesium oxide, alkaline earth oxides, other metallic oxides, asbestos, or inert materials may also be used as catalysts for the process. The best laboratory results gave yields of 82 per cent of the theoretical of phthalic anhydride free from chlorides, nitrates, etc.

Developments immediately subsequent to the announcement of the original process were concerned primarily with getting a pure product. A patent claiming as an article of manufacture phthalic anhydride in the form of long colorless needles and melting above 130° C.[19] served to show the progress that had been made up to that time by stimulating a storm of protest. The fact that phthalic anhydride in the form of long, colorless,

[17] Gibbs. *J. Ind. Eng. Chem.* 11, 1031 (1919).
[18] a. Gibbs and Conover, U. S. Pats. 1,284,888 (1918), 1,285,117 (1918) (Application 1917) dedicated to the public; Brit. Pat. 119,517-8 (1917); *see also* b. Gibbs, Brit. Pat. 14,150-1 (1917); Can. Pat. 186,444-5 (1918); U. S. Pat. 1,288,431 (1918); 1,303,168 (1919); c. Selden Co., Brit. Pat. 170,022 (1920).
[19] U. S. Pat. 1,336,182 (1920) Andrews assr. to Selden Co.

glistening needles, substantially chemically pure and having a melting point above 130° C. was being manufactured by several concerns by the different processes at the time of the application was clearly shown.[20, 6] Disclosures in the prior literature caused the patent to be declared invalid.

The development of this process for the air oxidation of naphthalene to phthalic anhydride constitutes one of the outstanding triumphs of American technical men. The pioneer work of Gibbs and his associates opened up an entirely new field of scientific and commercial development, and contributed largely to the development of vat dyes of the anthra-
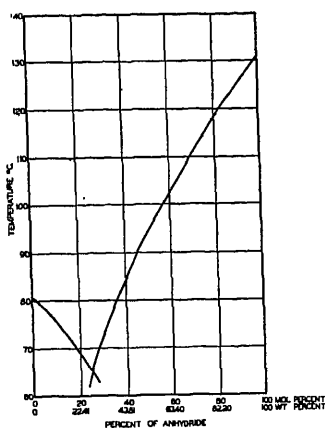
Fig. 40.—Freezing point curves for the system phthalic anhydride - naphthalene (Monroe).[20a]
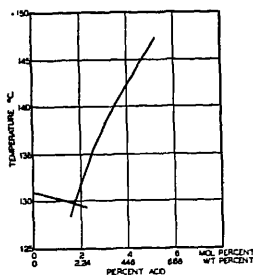
Fig. 41.—Freezing point curves for the system phthalic acid-phthalic anhydride (Monroe).[20u]

quinone series. Perfection of the details of the process especially in the fields of catalysts and temperature control has resulted in the accumulation of a mass of patent literature to which reference must be made for information.

Mechanism of the reaction. At ordinary temperatures naphthalene is inert to oxygen and at high temperatures burns with a smoky flame. The final products of combustion are, as usual with hydrocarbon oxidation, carbon dioxide and water. Its heat of combustion is 1,233,000 gram calories per gram mol at 20° C. Studies on the mechanism of combustion have shown that a stepwise process involving successive amounts of oxygen is effective.

The main stages of this oxidation of naphthalene may be represented by the following reactions:

[20] a. Monroe, *Ind. Eng. Chem.* 11, 1116 (1919); b. Bebie, *ibid.* 13, 91-2 (1921); c. Monroe, *ibid.* 14, 1085 (1922).

naphthalene — alpha-naphthaquinone

$$+ 3O \longrightarrow + H_2O \tag{1}$$

alpha naphthaquinone — phthalic anhydride

$$+ 6O \longrightarrow + 2CO_2 + H_2O \tag{2}$$

phthalic acid

$$+ H_2O \longrightarrow \tag{3}$$

naphthaquinone — benzoic acid

$$+ 6O \longrightarrow + 3CO_2 \tag{4}$$

phthalic acid — benzoic acid

$$\longrightarrow + CO_2 \tag{5}$$

naphthaquinone   maleic anhydride

$$+ 15O \longrightarrow \qquad + 6CO_2 + 2H_2O \qquad (6)$$
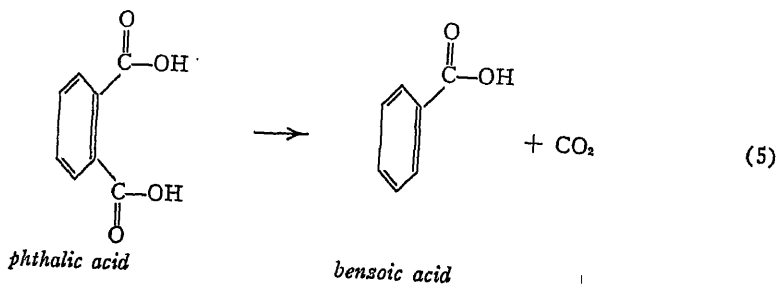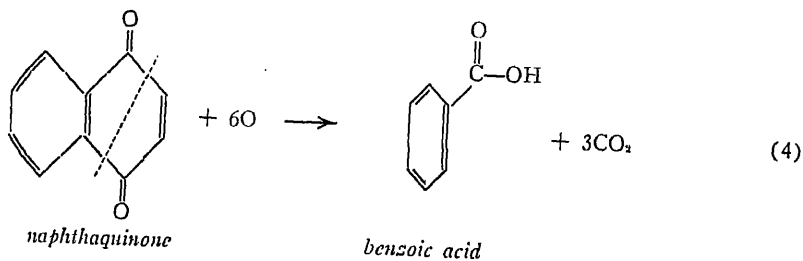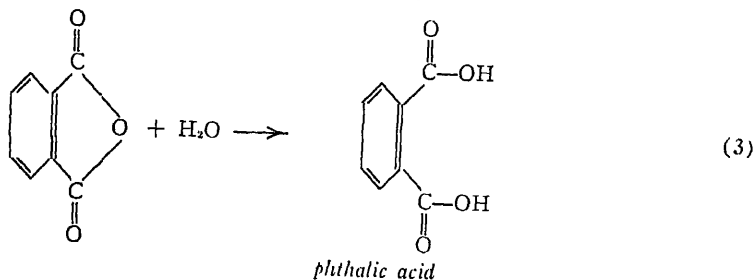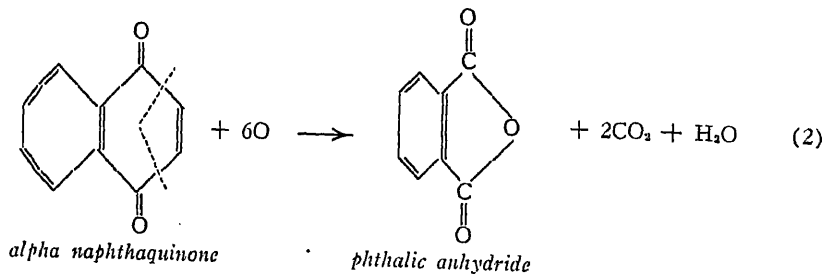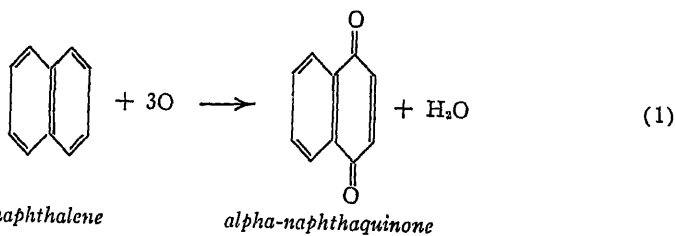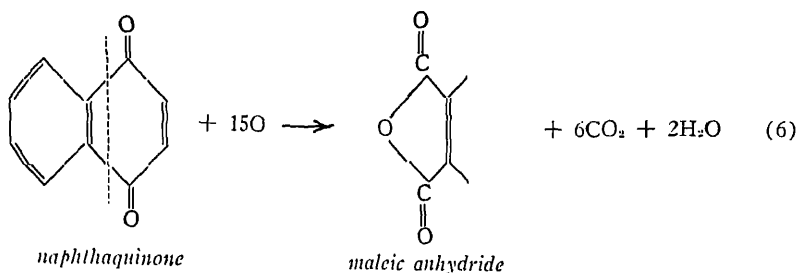
Many of the intermediate steps have of necessity been omitted from this series of reactions. It is probable that the initiation of reaction is through the hydroxyl stage as in the case of benzene oxidation, and that the stepwise oxidation of the naphthalene ring to phthalic anhydride proceeds through somewhat the same mechanism as is postulated for the breakdown of the benzene ring in the formation of maleic anhydride. The fact that naphthaquinone is the complete analog of ordinary quinone, having a similar odor, being volatile with steam, and giving similar reactions, makes probable the change in structure of the naphthalene ring as shown in the transition to phthalic anhydride.

The formation of naphthaquinone marks one of the points of resistance in the oxidation of naphthalene. The stability of naphthalene is such that under ordinary conditions of temperature (up to 400° to 500° C.) a catalyst is necessary to institute oxidation. Results of investigations, however, have shown that the presence of a hydroxyl group on the naphthalene ring greatly increases its activity toward oxygen as well as toward other reagents and facilitates the introduction of other atoms or groups into the ring. Because of these facts, the reaction can hardly be expected to stop at the naphthol stage even on the theoretical ground that it represents one of the steps in the process. Indeed, the presence of naphthols in the reaction products has only been qualitatively reported as very small in amount. However, when the temperature of the catalyst mass is properly controlled and the time of contact properly adjusted, good yields of naphthaquinone are possible. With a catalyst composed of pumice on which 10 per cent by weight of vanadium pentoxide had been deposited, yields of 25 per cent of the theoretical of naphthaquinone could be obtained. The conditions of operation in this case were at a temperature of 418° C. for the lead bath in which the catalyst tube was immersed, an air ratio of 6.5 times that necessary for complete combustion, and a time of contact of 0.13 second.[21] It is highly probable that by altering conditions somewhat, much better yields could be obtained. Even under conditions that favor phthalic anhydride formation, i.e., a lower air ratio and longer time of contact, naphthaquinone will appear in the product if the temperature is allowed to fall or the time of contact to become less.

[21] Ho, Thesis (1930) Chem. Eng., Mass. Inst. of Tech. Cambridge, Mass.

The fact that the alpha position of the aromatic compounds is the most reactive accounts for the formation of alpha-naphthaquinone to the practical exclusion of the two other naphthaquinones theoretically possible. This structure is the only comparatively stable configuration before ring destruction.

If the catalyst used is active enough, and the conditions of temperature and time of contact sufficiently severe, the naphthaquinone step is passed and ring rupture occurs. Then the next point of resistance is the rupture of the remaining benzene ring and phthalic anhydride becomes the predominating product. Derivatives of benzene with hydrocarbon side chains in the ortho position are very readily oxidized to phthalic anhydride no matter what the configuration or length of the chains may be. An examination of the naphthalene or naphthaquinone ring shows that it may be considered as a derivative of benzene with substitutions in the ortho position. This indicates that it should be possible to easily oxidize to the phthalic anhydride stage. However, the ring structure offers some resistance to rupture and a total of six atoms of oxygen must be reacted before the phthalic anhydride stage is reached from the naphthaquinone stage. This makes it essential for longer times of contact to be used to allow for the completion of the intermediate steps. Cleavage of the ring occurs principally across the single linkings in the meta position and leaves the double linking intact for the maleic or phthalic anhydride structure. However, this cleavage does not occur exclusively, since some splitting also occurs through single linkings in the para position to each other and results in the formation of benzoic acid. Benzoic acid might also result from the splitting of carbon dioxide from phthalic acid although this view might be objected to since the temperature of reaction is such that any phthalic acid would have but a transient existence if present at all, at the temperatures used in the process. However, actual experiment has shown that benzoic acid and maleic anhydride result from the further oxidation of phthalic anhydride. For instance, if a mixture of 8 parts of air and one part of phthalic anhydride by weight is passed over a vanadium oxide catalyst at 425° C. and with a time of contact of 0.4 second, about 53 per cent of the phthalic anhydride undergoes complete combustion and conversion to maleic anhydride.[22]

The resistance of the benzene ring to cleavage is such that phthalic anhydride may be obtained in good yield by suitably regulating operating conditions. Published data, representing the results of experiments with vanadium pentoxide catalysts at a temperature range of 400° to 500° C. and an air ratio of from 1 to 3 times that theoretically necessary for complete oxidation, show the presence of the following products:

Phthalic anhydride .... 60 to 85 per cent of theoretical
Unreacted naphthalene .... none to 25 per cent
Complete combustion .... none to 25 per cent

[22] U. S. Pat. 1,489,741 (1924) Craver assr. to Barrett Co.

Maleic anhydride .... none to 25 per cent
Naphthaquinones .... very small amounts under proper condi-
                                tions for phthalic anhydride
Naphthols .... very small in amount
Acrylic acid .... uncertain
Benzoic acid .... uncertain (at least 1 per cent)
Ethylene .... uncertain
Carbon dioxide .... largest constituent of gas
Carbon monoxide .... none

In the oxidation of the naphthalene ring then, it is seen that three types of reactions are controlling: First, the addition of oxygen to the ring, second, the destruction of the naphthalene ring, and third, the destruction of the benzene ring. Theoretically, it should be possible to stop at any of the intermediate steps but actually only the points of major resistance may be depended upon to allow isolation of intermediate oxidation products. From the existing data it is impossible to determine the reaction rates of the different steps and the presence of catalysts would make any ordinary presentation difficult even with more data than are available.[28]

Carbon dioxide constitutes the main gaseous reaction product but is not found in quantities sufficient to account for the naphthalene unaccounted for in the oxidation. Carbon monoxide is not found in the gaseous products. These facts have led many of the investigators to believe that certain unknown gaseous products must be given off and in this way account for the poor naphthalene balances that have been obtained. However, most of the experimental work has been done with apparatus having an air cooled condenser tube attached directly to the reaction chamber for the collection of reaction products. Although this condenser remains sufficiently cool to condense the major part of the product, the various constituents present, especially unreacted naphthalene, will have appreciable vapor pressures at the temperatures of the condenser walls and because of the large volumes of air used in the oxidation considerable portions of material are swept into the atmosphere. This otherwise unaccounted for material may be collected by passing the exit gases through tubes of active charcoal and by considering this additional product to be unreacted naphthalene good carbon balances may be obtained under conditions where the balances would ordinarily have been poor.

Patent claims have been made for the formation of benzene and maleic anhydride with benzoquinone as a by-product by the oxidation of naphthalene.[24] For the formation of benzene an example is given in which a mixture of air and naphthalene vapor are passed over a vanadium oxide catalyst at 400° C., the reaction products cooled to 380° C. and then passed over a catalyst containing the oxides of cadmium and aluminum. For the formation of maleic anhydride a mixture of air and naphthalene vapor

[28] *Compare* Tronov, Popov, Kolotovkin and Stalash, *J. Russ. Phys. Chem. Soc.* 61, 2390 (1929), who claim that diphenyl and naphthalene react 1000 to 3000 times faster than benzene toward oxygen.
[24] Brit. Pat. 268,775 (1926) I. G. Farbenind.

is passed over a vanadium oxide catalyst at 400° C., the reaction products cooled to 390° C., passed over a catalyst of the oxides of zinc, cadmium, and aluminum, and then if required passed over a catalyst of the salts of vanadic acid at 410° C. after being mixed with preheated air. Besides maleic anhydride, benzoquinone is obtained as a by-product. The value of such a process depends upon the price differential existing between benzene and naphthalene.

Catalysts. The non-catalytic oxidation of naphthalene either in the liquid phase under pressure or in the vapor phase at atmospheric pressure, results in the formation of complete combustion products if temperatures high enough to give good reaction rates are used or else results in the formation of complex tars by condensations and polymerizations of intermediates if such low temperatures are used as to necessitate the use of long times of contact to obtain appreciable reaction. Hence, to obtain valuable products from the oxidation in commercial yields it is essential that catalysts be used.

In the vapor phase oxidation of benzene to maleic anhydride an active catalyst is necessary to force oxidation to rupture the ring without leading to complete destruction. Vanadium pentoxide or vanadium compounds such as tin vanadate have been successfully used for this purpose.[25] In the oxidation of alkylated benzene compounds to benzaldehyde, benzoic acid, or phthalic anhydride, a milder form of catalyst is effective. The oxidation of naphthalene to naphthaquinone would also require a mild form of catalyst to prevent ring rupture caused by too severe oxidation. However, oxidation to phthalic anhydride may be realized under ordinary conditions by the use of such catalysts as have been found effective in benzene oxidation, i.e., oxides of the metals of the fifth and sixth groups of the periodic system, especially the oxides of vanadium and molybdenum.

As more effective means of temperature and time of contact control have been developed it has been discovered that a great many materials are effective as catalysts for commercial operation. This is true because no matter what catalyst is used, the mechanism of the reaction is probably the same and it only remains to stop the oxidation at the proper point to obtain desired yields of intermediates. The less selective the catalyst is for the different steps the narrower is the zone of temperature and time of contact in which the desired reaction occurs and hence, the more strict must be the control in operation.

Consequently, a great number of materials have been proposed as catalysts for the reaction but as the majority of the information available is disclosed only in the patent literature and is concerned primarily with methods of preparation, it is impossible to compare them by means of operating data. That the oxides of molybdenum and vanadium are effective is evident from the early work on the process. Conversions of

[25] For reviews of vanadium catalysts *see* (a) Alexander, *J. Soc. Chem. Ind.* 48, 895-901 (1929); (b) *also* various articles in the "Vancoram Review" published by Vanadium Corpn. of America; (c) *also* Prandtl, "Die Literatur des Vanadins, 1804-1905."

naphthalene to anhydride of 80 per cent of theoretical are being realized on a commercial scale with vanadium pentoxide catalysts. These catalysts have a long life, functioning for over six months of continuous service and yielding up to 20,000 times their own weight of phthalic anhydride.[26]

Data in regard to catalysts of tin and bismuth vanadate are available from the work of Maxted,[27] who passed naphthalene vapor mixed with air over the catalysts contained in a U-tube * heated by a sodium-potassium
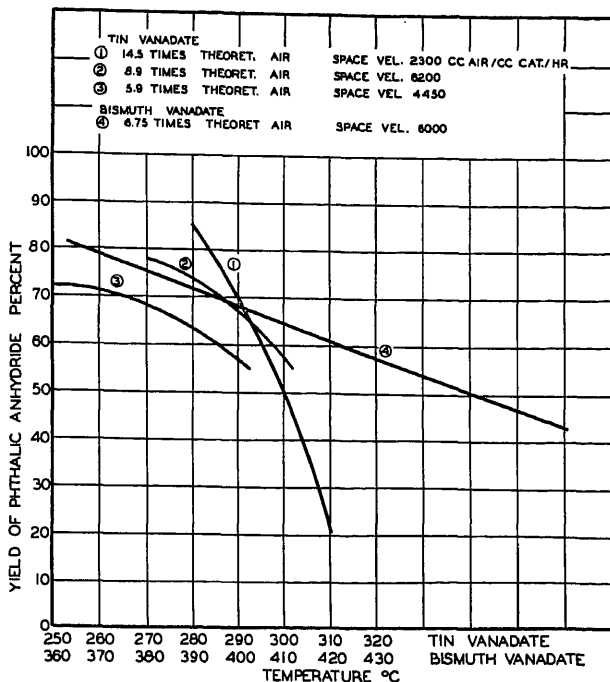
FIG. 42.—Naphthalene oxidation (Maxted).[27]

nitrate bath. Operation could be so controlled that either quinones or carboxylic acid anhydrides were formed. The tin vanadate catalyst became active at a relatively low temperature and at a bath temperature of 260° to 280° C. a brilliant deposit of phthalic anhydride crystals free from naphthaquinone was obtained. At temperatures lower than this, however, the product was colored yellow by the presence of the quinone. The bismuth vanadate catalyst showed the same characteristics but was effective at temperatures about 100° C. higher. At relatively high rates of flow, i.e., short times of contact, yields of 80 per cent by weight or higher were obtainable. From the shape of the curves shown in Figure 42 it is evident

[26] Downs, *J. Soc. Chem. Ind.* 45T, 188 (1926).
[27] Maxted, *J. Soc. Chem. Ind.* 47T, 101-5 (1928).
* *See* preceding chapter.

that optimum yields were not obtained especially at the higher air ratios. Although the curve of yield against bath temperature becomes steeper as the air ratio is increased, the possible yield of phthalic anhydride at correct temperature and time of contact becomes higher.

The tin vanadate catalyst prepared by precipitation and drying becomes active at an abnormally low temperature and is, hence, particularly effective in obtaining good yields since far-reaching secondary oxidation may be very largely prevented. It should be noted that the yields shown are based on one passage of the naphthalene vapor through the catalyst, all unreacted naphthalene being considered as lost. Although the bismuth salt becomes active only at a temperature 100° C. higher than the tin salt, the curve connecting yields at various bath temperatures is practically linear and the variation with temperature far less than with the tin salt. The space time yield at the higher rates of passage also exceeded 0.2 in the case of the bismuth salt indicating that it is a desirable material to use commercially. The decreased yields with both catalysts at the higher temperatures is due to complete combustion to carbon dioxide and water of a portion of the naphthalene.

Vanadium pentoxide in the form of a light powder prepared by decomposing ammonium metavanadate at low temperatures is an excellent catalyst for oxidation to phthalic anhydride.[9] Fused vanadium pentoxide is an even better catalyst.[28] This is shown by the data of Conover and Gibbs which furnishes a basis of comparison. Thus, a catalyst of light, fluffy V_2O_5 made from ammonium metavanadate by heating at temperatures below 300° C. converted 50.6 per cent naphthalene to phthalic anhydride per pass with a yield of 68.8 per cent of the naphthalene attacked. Vanadium pentoxide prepared from the same ammonium metavanadate and fused at temperatures above 650° C. gave a conversion of 61.2 per cent and a yield of 80.1 per cent, showing greater activity under the same experimental conditions. Although these results are not definitely conclusive since the conditions of the experiments were not varied over a wide range, they indicate the desirability of using fused or sintered vanadium oxide as a catalyst for this reaction. Molybdenum oxide is a fairly good catalyst, having a somewhat lower activity than vanadium pentoxide. Both of these materials as well as the tin and bismuth vanadate catalysts used by Maxted, show good resistance to poisons such as arsenic trioxide and sulfur dioxide.

Supported vanadium oxide catalysts may be prepared by either mixing powdered pumice with a solution of ammonium vanadate and subsequently drying, by soaking pumice in a gum solution and then shaking with ammonium vanadate powder, by impregnating porous material with a colloidal solution of vanadic acid stabilized with starch, blood, etc., or by precipitating the oxide on the porous support from solutions of the salt.[20]

[28] U. S. Pat. 1,458,478 (1923) Gibbs.
[20] *See* Brit. Pat. 145,071 (1919) Wohl.

Molybdenum oxide catalysts are prepared by heating the ammonium molybdate or by depositing molybdic acid on inert supports. The oxide prepared from the ammonium salt is somewhat dark colored due to a certain amount of reduction caused by the hot ammonia. However, the degree of activity of this material as a catalyst is apparently independent of the method of preparation, degree of oxidation, or supporting material. Yields of only about 50 to 60 per cent of theoretical as phthalic anhydride are obtainable with this catalyst. Molybdenum oxides have the added
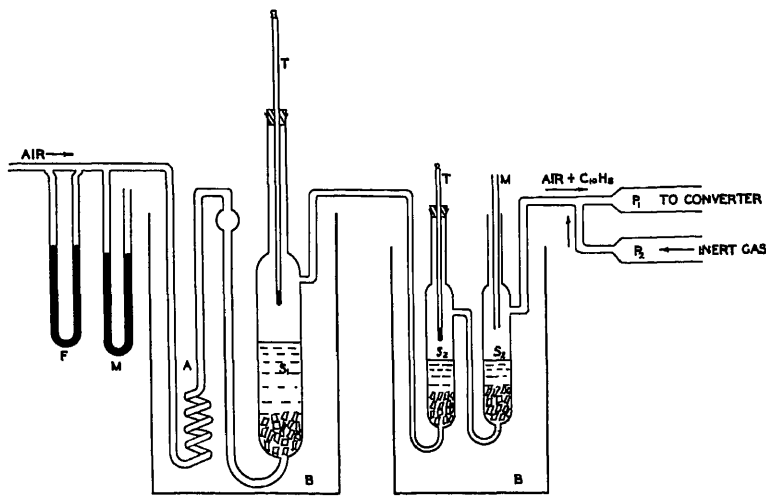
Fig. 43.—Saturater for constant air-naphthalene mixtures.

F = Flowmeter
A = Air preheater
S_2 = Saturater
P_2 = Inert gas preheater
B_2 = Oil thermostat

M = Manometer
S_1 = Presaturater
P_1 = Preheater
B_1 = Oil bath

Note: All connecting tubes are electrically heated and lagged with magnesia (not shown in figure).

objectionable feature of being somewhat volatile at the temperature of reaction and, hence, introduce the factors of catalyst loss and product contamination. Mixed catalysts composed of vanadium oxides with added amounts of molybdenum oxides give good results.[30]

Vanadium oxide catalysts, fused or supported, as are used in practice today become active at a temperature of about 270° to 280° C., are very active at 320° to 330° C., and do not induce decomposition or complete combustion at temperatures as high as 400° C. unless very long times of contact are permitted. The temperature range within which good operating results may be obtained is thus very wide, a factor that contributes quite largely to the applicability of this material to commercial operation.

[30] Kusama, *J. Chem. Soc. (Japan)* 44, 605 (1923).

Although certain materials may give excellent results on a laboratory scale where temperature control is rigid, they are not at all useful to quantity production since on a large scale it is much more difficult to control temperature at a constant value and to obtain a uniform and small temperature gradient throughout the catalyst mass, a point of great importance. Nevertheless, it is quite possible to duplicate laboratory results with properly designed manufacturing apparatus.

Many modifications of the vanadium catalysts have been developed. Thus, by fusing vanadium pentoxide with infusorial earth a more active
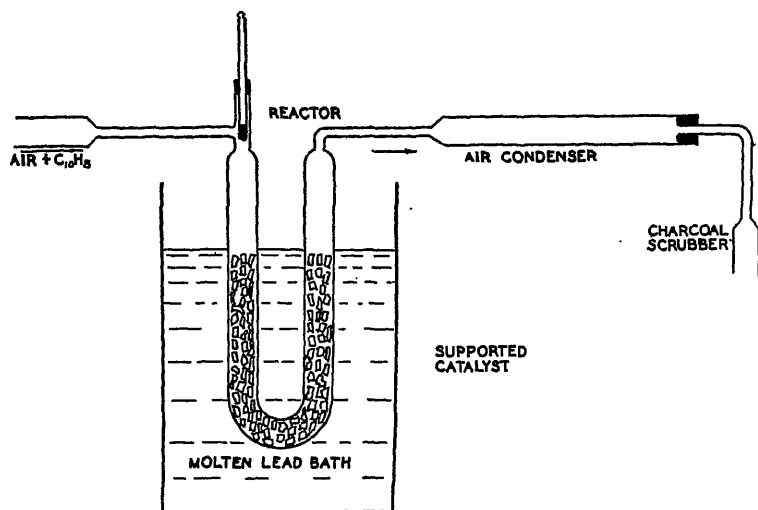
Fig. 44.—Reactor and condenser for naphthalene oxidation.

and physically rugged catalyst may be formed.[31] Vanadium pentoxide catalysts may be promoted by the addition of acidic oxides such as oxides of molybdenum, tungsten, cerium, chromium, or uranium, to the catalyst, or sulfur dioxide to the reacting gases,[9] but not basic oxides since they supposedly combine with the acid as it is formed and give rise to undesired decomposition.[32] Oxides of vanadium lower than the pentoxide are prepared as catalysts by impregnating pumice with a solution of vanadyl oxalate obtained by dissolving vanadic acid in oxalic acid, and then heating to 270° C.[33] The lower oxides of vanadium produced by this method are, however, changed to a mixture of V_2O_4 and V_2O_5 during the oxidation operation. Mixtures of vanadium pentoxide and metallic pyro-vanadates are suitable catalysts for various organic and inorganic oxidations.[34]

[31] U. S. Pat. 1,463,206 (1920) Gibbs assr. to E. I. duPont deNemours & Co., Inc.
[32] Kusama, *Bull. Inst. Phys. Chem. Research* (*Tokyo*) I, 1087-1132; Abstr. section 1, 105-6 (1928).
[33] French Pat. 646,263 (1927) Kuhlmann.
[34] French Pat. 635,717 (1927) Monsanto Chem. Co.

Vanadium may be used as a homogeneous catalyst in the form of vanadyl chloride, $VOCl_3$, by passing a mixture of hydrocarbon vapor, air, and chloride through a tube containing such inert materials as pumice, brick, etc., and maintained at a temperature of 300° to 650° C. Any products of the decomposition of the $VOCl_3$ which accumulate in the reaction zone may be removed and reconverted by phosgene or the vapor of carbon tetrachloride at a temperature of about 300° to 350° C. Such low concentrations as one gram of $VOCl_3$ per 100 liters of the secondary air are used.[35] It is not clear whether this process represents a case of homogeneous catalysis or whether the material deposits on the inert filler and acts as a heterogeneous catalyst.[36]

The extremely active character of the vanadium oxide catalysts necessitating very careful time of contact control at the higher temperatures to prevent undue losses to maleic anhydride and complete combustion products may be modified by the addition of certain proportions of the oxides of the less active metals,[37] such as manganese, uranium, copper, cobalt, chromium, etc. In keeping with the findings of Kusama and Gibbs it was found that the use of admixed oxides of metals more basic than those of the fifth and sixth groups of the periodic system such as those of sodium, copper, lead, cobalt, aluminum, cadmium, etc., tended to increase the relative amounts of maleic acid formation and complete combustion. The preparation of these mixed catalysts may best be accomplished by either simultaneous precipitation from a solution of the salts or by mixing the oxides or hydroxides in water suspension.[38]

The oxides of magnesium, aluminum, silicon, titanium, zirconium, cerium, columbium, chromium, tungsten, uranium, manganese, iron, nickel, cobalt, copper and finely divided platinum mixed with magnesium oxide are poor or worthless catalysts. Coal heated in air for some time at 200° to 300° C. has been claimed as an oxidation catalyst for the conversion of alcohol to aldehydes, toluene to benzaldehyde, naphthalene to naphthaquinone and phthalic anhydride, etc., at temperatures up to 300° C.[39] The use of ferric oxide as a catalyst for naphthalene oxidation in the presence of alkalies by heating in solution was mentioned in 1902 together with vanadium compounds.[40] Titanium oxide catalysts require promotion by the addition of nitrogen oxides to the reacting gases in a concentration of 2 per cent in order to promote oxidation of naphthalene to phthalic anhydride.[41] This procedure, of course, is open to the objection that nitrogen compounds are formed which are difficult to separate from the product.

[35] Brit. Pat. 164,785 (1921) British Dyestuffs Corpn., Ltd.
[36] a. Green and Green, Brit. Pat. 183,044 (1928); French Pat. 554,178; b. Downs and Weiss, U. S. Pat. 1,355,098 (1918); 1,374,721 (1919).
[37] U. S. Pat. 1,489,741 (1924) Craver to Barrett Co.
[38] Miscellaneous references to vanadium catalysts: a. Gibbs, U. S. Pat. 1,463,206 (1923) to E. I. duPont de Nemours & Co., Inc.; b. Selden Co., French Pat. 642,362 (1927) purification of crude vanadate solutions by oxidation; c. Jaeger, U. S. Pat. 1,678,626-7 (1928) to Selden Co. revivifying catalysts by treatment with H_2O_2 or SO_3.
[39] Ger. Pat. 203,848 (1908) Dennstedt and Hassler-Control of products by variation of air ratio is also mentioned.
[40] Bodländer, Z. Elektrochem. 9, 732-3 (1903).
[41] Brit. Pat. 182,843 (1922) Atack assr. to British Alizarine Co., Ltd.

That aluminum oxide is but an inactive catalyst toward the oxidation is shown by the experimental data obtained with it. When a mixture of one part of naphthalene with 16 parts of air by weight is passed through a tube containing aluminum oxide maintained at about 450° C. at such a rate that the time of contact is about 0.4 second, a yield of only 12.5 parts of phthalic anhydride and 5 parts of naphthaquinone per 100 parts of original naphthalene is obtained.[42]

Siliceous or non-siliceous base-exchanging compounds have been proposed as catalysts either with or without the addition of active catalytic material.[43] Such catalysts as are composed of two-component zeolites obtained by the reaction of a silicate with a "metallate," i.e., tungstates, chromate, uranate, cerate, etc., or one or more metal salts have been claimed for a variety of reactions including the oxidation of aromatic compounds.[44] Non-siliceous base-exchanging compounds formed by the reaction of at least one compound such as a metallate, containing a non-siliceous anion capable of forming the acidic portion of the nucleus of a base exchange compound, with at least one compound such as a metal salt containing a metal element which is amphoteric in at least one of its oxidation stages to give a product alkaline to litmus and neutral or alkaline to phenolphthalein may be used for oxidation reactions. The utility of the large number of combinations possible in a catalyst of this type is not clear.[45a] The majority of the zeolitic combinations that have been proposed contain such catalytically active elements as vanadium, tungsten, molybdenum, chromium, uranium, copper, nickel, etc., and are presumably effective toward oxidation because of these elements.[45b]

Removal of heat from the reaction. In the vapor phase catalytic oxidation of naphthalene to phthalic anhydride, the heat of reaction is so great that unless it is rapidly and thoroughly dissipated the temperature of the catalyst mass rises to a point where complete combustion only occurs. Further, there is a tendency for the pentoxide of vanadium to be reduced to lower oxides at the high temperatures used, particularly if the oxygen supply is limited. These lower oxides tend to combine with the phthalic anhydride and subsequently decompose to destroy the anhydride, so that simple limitations of the oxygen supply to prevent further oxidation of the hydrocarbon is not effective.

The heat evolved in the oxidation of naphthalene to phthalic anhydride is shown by the following heats of combustion.*

$$C_{10}H_8(1) + 12O_2 = 10CO_2 + 4H_2O + 1{,}233{,}400 \text{ cal.}$$
$$naphthalene$$
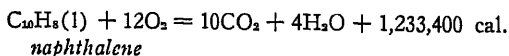
[42] U. S. Pat. 1,374,722 (1921) Downs assr. to Barrett Co.
[43] Brit. Pat. 315,854 (1928) Jaeger to Selden Co., also Brit. Pat. 279,466; Brit. Pat. 286,212 to Selden Co.
[44] Brit. Pat. 281,307 (1926) Jaeger to Selden Co.
[45] a. Brit. Pat. 286,212 (1927) Jaeger to Selden Co.; b. for other details *see* Brit. Pat. 295,270 (1927); French Pat. 649,292 (1927); U. S. Pats. 1,692,126 (1928); 1,694,122 (1928); 1,694,620 (1929) all to Selden Co.
* Kharasch, Heats of Combustion of Organic Compounds, *Bur. Standards J. Research* 2, Feb. (1929).

$$C_8H_4O_3(1) + 7\tfrac{1}{2}O_2 = 8CO_2 + 2H_2O + 784{,}500 \text{ cal.}$$
*phthalic
   anhydride*

$$C_{10}H_8(1) + 4\tfrac{1}{2}O_2 = C_8H_4O_3(1) + 2CO_2 + 2H_2O + 448{,}900 \text{ cal.}$$
naphthalene   phthalic anhydride
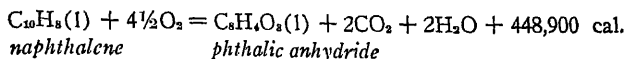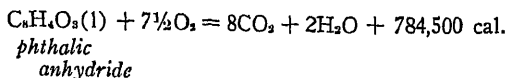
This means that for every pound of phthalic anhydride produced a total of 5460 B.t.u. of heat is liberated. In the early form of apparatus in which the catalyst was arranged in layers in a large converter, reaction heat present as sensible heat in the reaction vapors was used to heat the incoming mixture of naphthalene vapor and air by heat interchange in order to prevent undue cooling of the first portion of the catalyst layers by the cool reaction mixture. A blower delivered a rapid stream of air to a chamber containing molten naphthalene at a temperature of 90° to 130° C., depending on other conditions, and then to the heat interchanger. This gave a reaction mixture containing about ten times the air theoretically required for the reaction. Auxiliary cold air was admitted at intermediate points of the apparatus to lower the temperature whenever necessary. In this way a fair degree of temperature control could be exercised and the operation made practically autothermal. Radiation was depended on for the removal of heat in excess of that necessary for the operation.

However, this method of operation while satisfactory to a certain extent, especially when compared with the liquid phase, sulfuric acid method, does not insure uniform temperatures at the different catalyst layers nor in the catalyst mass itself. If the rate of flow of the vapor-air mixture is too slow most of the reaction occurs in the first catalyst layers and the excess of heat thus liberated in a confined zone causes the temperature to rise excessively with resultant losses by complete combustion and decomposition. The maintenance of a sufficiently rapid rate of gas flow prevents this sudden rise in temperature gradient and makes it possible to have a gradient that increases gradually to give the highest temperature near the exit end of the apparatus. This insures the combustion of undesirable intermediate compounds such as the naphthols, naphthaquinones, etc., which otherwise would contaminate the product and make separation more difficult, but without giving rise to any marked loss to complete combustion of phthalic anhydride.[30]

Dependence upon radiation for heat removal in the case of the old form of reactor was essential since even with the large excesses of air used the heat capacity of the total exit products was insufficient to remove the heat of reaction, especially when the air-naphthalene mixture had been preheated to approximately 350° C. prior to entering the catalyst zone. With the present method of temperature control and heat removal the heat of reaction amounts to about 10,000 B.t.u. per pound of naphthalene fed to the converter. As the proportion of naphthalene burned to com-

[30] See Kusama, *J. Chem. Soc. (Japan)* **44**, 605 (1923) for experimental data on temperatures.

plete oxidation products increases this heat evolution increases. In the old type of converter with the catalyst on trays this would result in temperature rises leading to further combustion and giving a self-accelerating effect. The converse is also true, since as the amount of heat released decreased the temperature dropped, reaction slowed up, and the oxidation was not complete. These two extremes, therefore, could result in either greatly increased total combustion or in decreased oxidation leading to a badly contaminated product.

In operation, this shelf type of converter was manually controlled by regulation of the cold air valves between the catalyst shelves with minute to minute observations of pyrometers by the operator of each converter. The largest of these converters apparently could produce about 50 pounds of phthalic anhydride per 24 hours on good days. A boiling mercury controlled converter of approximately the same overall dimensions can produce 1800 pounds of phthalic anhydride per 24 hours, and one operator can control about eight or more of these machines.*

The design of a converter that will effectively remove the reaction heat and control the temperature is a special problem requiring consideration of reaction rates, heat transfer, temperature control, time of contact of reactants with catalyst, materials of construction, etc. It will, hence, be discussed in a separate section. Although converters have been built and operated successfully, such processes have many undesirable features such as cumbersome construction, the necessity for using baths of metals or salts, etc.

The very large excesses of air that are used in the vapor phase processes for aromatic oxidation are effective in absorbing a portion of the heat of reaction as sensible heat, as well as in diluting the reacting vapors of hydrocarbon and thereby preventing condensations and polymerizations between the intermediately formed compounds. The value of this excess of air, amounting to as high as 6.5 times that theoretically required for complete oxidation in some of the experimental work, in insuring rapid reaction rates and hence, short times of contact to give good yields of anhydride free from by-products has been shown. The use of high proportions of inert gas would, however, tend to have the opposite effect on reaction rates and the use of excessive quantities of air would promote complete combustion with consequent loss of raw material. Hence, it is difficult to see how this dilution principle could be carried any farther than is done at present. The largest possible value of such use of diluents would possibly lie in the production of such an intermediate as naphthaquinone which requires but a small amount of oxidation for its formation.[46]

Practically the use of sufficient air or inert gas such as flue gas to remove all of the heat generated in the reaction zone would necessitate

* Private communication from Mr. J. M. Weiss.
[46] U. S. Pats. 1,439,500 (1922) 1,377,534 (1921) to Barrett Co.

about 250 mols of gas per mol of naphthalene oxidized to phthalic anhydride. The use of such amounts of inert gas would be objectionable on a commercial scale because of the excessive gas volumes that would necessarily have to be handled, the large equipment necessary to obtain commercial production and the difficulties that would attend recovery of product because of the great dilution. Absorption methods of recovery would probably be resorted to, such as scrubbing in alkaline solutions.
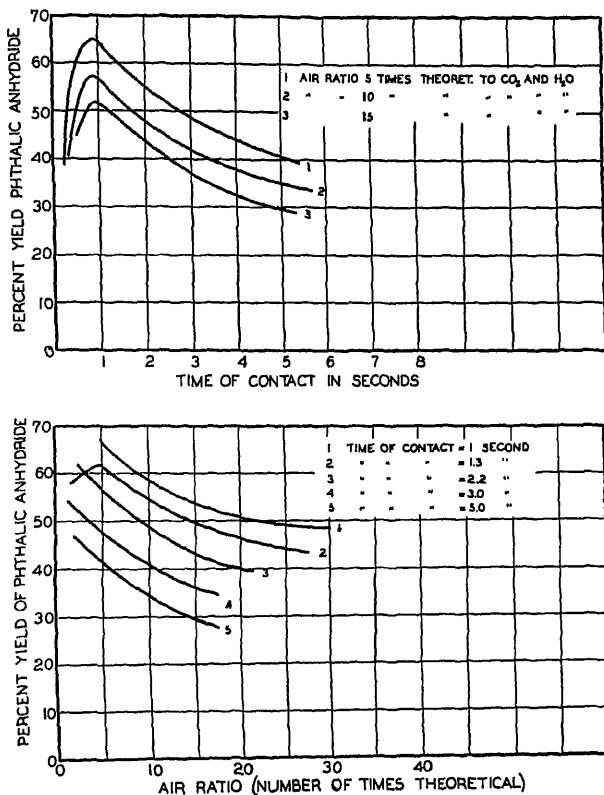
Fig. 45.—Effect of air ratio on oxidation of naphthalene (Ho).[21]

Subsequent recovery of anhydride would then be expensive and troublesome.

Methods have been proposed which involve the injection of a spray of water between successive catalyst zones.[47] The vaporization of the water removes heat from the hot gases and prevents the temperature from rising abnormally. Such methods are relatively unsatisfactory, however, because the temperature is not maintained at the uniform value for optimum conditions of operation.

[47] Brit. Pat. 249,973 (1925) Green.

Although baths of molten metal, or salts, have been used for removing reaction heat, the most satisfactory method has been to remove the heat as latent heat of evaporation of a liquid boiling at the proper temperature.

Recovery of Phthalic Anhydride.

According to the present method of operation, the products from the converter are passed continuously to a condenser where phthalic anhydride is first condensed in a relatively pure condition. The impurities having higher vapor pressures must be cooled further and condense in later sections. Without shutting down the converter the products are periodically
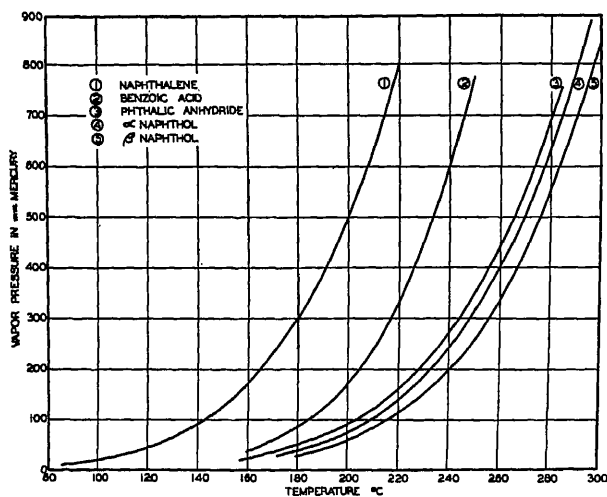
FIG. 46.—Vapor pressure curves for constituents of the product from the oxidation of naphthalene. (I.C.T.)

collected from the condenser system and purified. Phthalic anhydride may be purified by resublimation or by vacuum distillation in a column. Further chemical treatment has been used and proposed to aid in the removal of impurities.

Phthalic anhydride may be separated from the reaction products from the oxidation of naphthalene by a process of sublimation. Water from the reaction and unreacted naphthalene pass over at a lower temperature than the anhydride and may be separated quite completely from it. The anhydride may next be separated from the naphthaquinone and other colored materials which remain in the retort. In this way pure, crystalline phthalic anhydride may be obtained quite readily. The separation by fractionation may also be accomplished by vaporizing the reaction product into a flowing stream of air or cleaned flue gas at a temperature of about 200° C. and then cooling in chambers at successively lower temperatures.

In this way the components of the mixture may be separated according to their vapor pressure.[48]   The naphthols, however, have a vapor pressure very nearly that of phthalic anhydride and would be difficult to separate from the pure product.   Although occurring in only small amounts during improper operation, the formation of naphthols must be guarded against by insuring proper air ratios, temperatures and times of contact.[49]

It is also possible by a process of crystallization from carbon tetrachloride solutions that have been clarified and decolorized by active charcoal to obtain crops of anhydride crystals free from naphthalene which remains dissolved in the carbon tetrachloride.[50]

Neither of these simple processes completely free the phthalic anhydride of all impurities and in order to obtain a compound sufficiently pure to give brilliant dye stuffs, it is necessary for other treatments to be used. This is particularly true of such operations that use the cruder grades of naphthalene.

The impurities in phthalic anhydride obtained in the vapor phase oxidation process may be caused to condense or polymerize by heating either with or without the addition of special agents.   The vapor pressure of these materials is so lowered by this treatment that subsequent sublimation of the mass results in pure product, the condensed materials remaining in the retort.

For this purpose phthalic anhydride is heated in a closed retort either to the boiling point or to a somewhat lower temperature in the range 180° to 280° C. for a period varying from 2 to 10 hours depending on the grade of material and the temperature of treatment.   Superheated steam is injected at the end, the pressure allowed to drop, and the phthalic anhydride distilled off.[51]   Various condensation and polymerization catalysts may be added to the heated mixture such as zinc chloride,[52a] manganese dioxide, silica, zeolites, together with superheated steam,[52b] manganese dioxide on pumice.[52c]   The different impurities may be selectively halogenated[53] by heating the phthalic anhydride for several hours near the boiling point with manganese dioxide and chlorine.   In this way polymerization and condensation of the unsaturated impurities is facilitated and much higher boiling point compounds made from them which remain in the retort during the subsequent distillation of the phthalic anhydride.   The reaction mixture even prior to separation of the products may be passed in the vapor state before condensation over solid, inert substances such as pumice,

[48] Andrews, U. S. Pat. 1,685,624 (1928) assr. to Selden Co.
[49] a. Alpha naphthaquinone, m.p. 125° C., begins to sublime at 100° C.   Although but slightly soluble in cold water, steam distills readily at 100° C.   It is soluble in hot alcohol, and in alkaline solutions.   Grove, J. Chem. Soc. 26, 210 (1873); Ann. 167, 358 (1873); b. By heating 2.9 grams of α-naphtha quinone at 115° to 120° C. at a pressure of 12.5 mm. mercury for 1.5 hours, Kempf was able to obtain but 0.67 grams of sublimate.   Kempf, J. prakt. Chem. (2), 28, 236, 257 (1908).
[50] U. S. Pat. 1,301,388 (1919) Conover and Gibbs.
[51] Can. Pat. 284,272 (1928) Jaeger and Conover assrs. to Selden Co.
[52] a. U. S. Pat. 1,728,225 (1929) Bowers to E. I. duPont de Nemours & Co., Inc.; b. Brit. Pat. 285,017 (1927); French Pat. 647,880 (1928) Selden Co.; c. Brit. Pat. 284,017 (1927) Jaeger and Canon to Selden Co.
[53] U. S. Pat. 681,238 (1928); U. S. Pat. 1,702,871 (1929); Brit. Pat. 285,017 (1929) Jaeger assr. to Selden Co.

silica gel, active carbon, bauxite, iron turnings, etc., to effect a purification.[54]

Claims for the liquid phase oxidation of naphthols in the presence of alkalies by means of cupric oxide [55] suggest that the small amounts sometimes present in the phthalic anhydride product are acted on in a similar way by the manganese dioxide and other oxidizing agents claimed in the purification processes.

Aldehydic reacting material such as trioxymethylene is added to the crude phthalic anhydride in a refining operation. Subsequent boiling of the mixture followed by the volatilization and fractional condensation of the anhydride results in a removal of certain undesirable constituents.[56]

Synthetic anthraquinone. The advent of cheap phthalic anhydride in a very pure form and the production of pure aluminum chloride [57] in large quantities at low cost have made it possible for American manufacturers to synthesize the anthraquinone necessary for the manufacture of dyes in competition with those from anthraquinone obtained by the oxidation of anthracene as practiced in England and Germany. Today, synthetic anthraquinone and anthraquinone derivatives furnishes a large outlet for phthalic anhydride.

The formation of anthraquinone from phthalic anhydride and benzene by the Friedel and Crafts synthesis is conducted in the presence of aluminum chloride.[58] Ortho-benzoyl benzoic acid is first formed and then

phthalic anhydride   *o-benzoyl benzoic acid*

o-benzoyl benzoic acid   *anthraquinone*
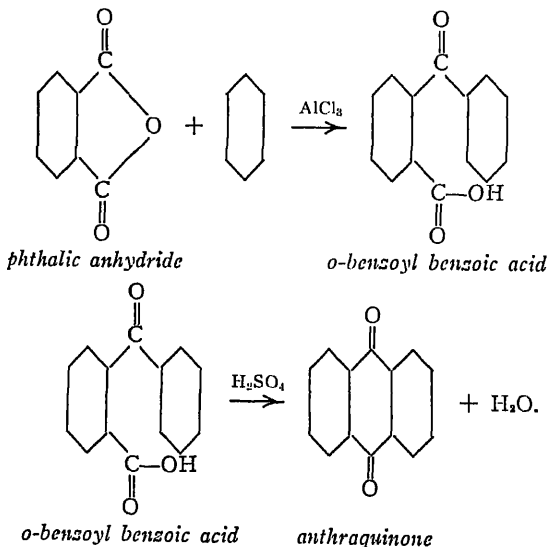
[54] a. Brit. Pat. 272,557 (1926) I. G. Farbenind; b. U. S. Pat. 1,693,915 (1928) Brode and Johannsen assrs. to Grasselli Dyestuffs Corpn.
[55] U. S. Pat. 702,171 (1902); Brit. Pat. 15,527 (1901); French Pat. 313,187 (1901) to Basle Chem. Works.
[56] U. S. Pat. 1,755,242 (1930) Conover assr. to Monsanto Chem. Works.
[57] McAfee, *Trans. Am. Inst. Chem. Eng.* 22, 209 (1929); *Ind. Eng. Chem.* 21, 670-3 (1929).
[58] A historical review of synthetic anthraquinone is given by Phillips, *Chem. Rev.* 6, 157 (1929).

dehydrated to anthraquinone. Other catalysts such as ferric chloride or mixtures of ferric chloride and aluminum chloride may also be used.[59]

The o-benzoyl benzoic acid is prepared by mixing phthalic anhydride with an excess of benzene and adding to an amount of aluminum chloride equimolar to the anhydride used. This mixture is maintained at a temperature of 35° C. in a lead lined kettle, jacketed for steam heating, for about half an hour. The temperature is then slowly raised to the boiling point of benzene and maintained until hydrochloric acid is no longer evolved. Benzene is removed by distillation with steam, the o-benzoyl benzoic acid dried and converted to anthraquinone by treatment with 95 to 98 per cent sulfuric acid at a temperature of from 110° to 150° C. for three-quarters to one hour. The anthraquinone thus formed is recovered from the concentrated sulfuric acid by careful dilution of the acid with water or treatment with steam to obtain large crystals to facilitate filtration, removal of acid, and washing.

The anthraquinone so obtained is purified by sublimation. Although various modifications of this process have been introduced, the basic principles remain the same.[60] The yield of o-benzoyl benzoic acid is about 95 per cent of theory or 145 per cent of the weight of phthalic anhydride used. The overall yield of sublimed anthraquinone on the phthalic anhydride used is more than 120 per cent by weight, or 85 per cent of theory.

Synthetic anthraquinone has had an advantage over that produced by the chromic acid oxidation of anthracene in having a greater purity and in giving more brilliant colors to the resulting dyes.[61]

TABLE XL.—*Anthraquinone Produced in the United States.*[1]

Year	Pounds	
1919	294,260	
1920	539,619	
1921	125,358	
1922	395,107	
1923	857,910	(about 50 per cent synthetic)
1924	638,755	(about 75 per cent synthetic)
1925–1926	Figure not revealed	

For certain dyestuffs a supply of 2-methyl anthraquinone is necessary. As crude coal tar contains but a small amount of methyl anthracene not readily available, it is necessary for the 2-methyl anthraquinone to be made synthetically. This can be done in a manner similar to that used for synthetic anthraquinone with toluene in place of benzene. Phthalic anhydride is condensed with toluene in the presence of aluminum chloride to obtain the tolyl benzoic acid. This acid after being dried is heated in strong sulfuric acid at an elevated temperature for several hours to form

[59] a. Gallay and Whitby, *Can. J. Research* **2**, 31 (1930); b. Boswell and McLaughlin, *ibid*, **1**, 400-4 (1929); c. Groggins, *Ind. Eng. Chem.* **23**, 152-60 (1931).
[60] Ger. Pat. 495,447, 499,587 (1927) I.G. Farbenind.
[61] Groggins, *Chem. Markets* **26**, 479 (1930) gives cost figures on synthetic anthraquinone manufacture.

2-methyl anthraquinone. By pouring the hot sulfuric acid solution into hot water to dilute, the methyl anthraquinone separates in a readily separable form.[62] The use of cold water to dilute the sulfuric acid solution for the purpose of precipitating the methyl anthraquinone results in a very fine suspension, difficult to filter.

The condensation of phthalic anhydride with chlorobenzene is used to produce chloroanthraquinone for the manufacture of aminoanthraquinone.

Naphthanthraquinone may be prepared by the condensation of phthalic anhydride and naphthalene in the presence of aluminum chloride to alpha naphthoyl benzoic acid and the subsequent dehydration of the alpha naphthoyl benzoic acid with sulfuric acid.[63] To obtain high yields of product in the proper condition of purity necessitates somewhat different procedure

phthalic anhydride naphthalene   *α naphthoyl benzoic acid*

naphthanthraquinone (1,2-benzanthraquinone)
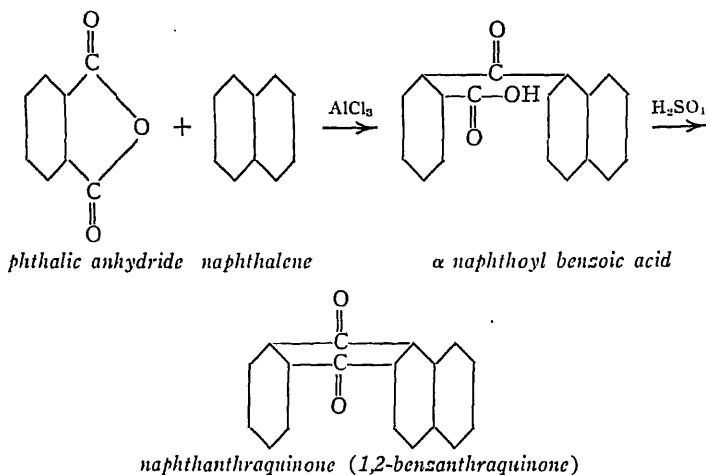
than in the case of anthraquinone synthesis. The development of such a practical process has been too recent to make possible an estimate of industrial interest.

Preparation and Separation of Benzoic Acid from Phthalic Anhydride

The small amount of benzoic acid that forms with the phthalic anhydride during the oxidation of naphthalene represents a waste when not recovered. Methods have been proposed for the separation of the two acids which depend on differences in solubility and vapor pressure. Thus, an aqueous dispersion of the two acids is subjected to the leaching action of a solvent for the benzoic acid, such as gasoline or benzene. The solvent is subsequently separated from the water layer and the acids recovered

[62] U. S. Pat. 1,515,325 (1924) Bailey to the Barrett Co.
[63] Groggins and Newton, *Ind. Eng. Chem.* 22, 157 (1930).

from the separate layers by evaporation.[64] Or the mixed acids may be steam distilled at a temperature slightly above that at which the phthalic acids are transformed into anhydrides, i.e., 150° to 175° C. Benzoic acid is then distilled from the phthalic acid and may be recovered by fractional condensation from the vapors or by evaporation from the total condensate.[65] Treatment of the benzoic acid-phthalic anhydride mixture with the vapors of an organic solvent for benzoic acid at a temperature at which the benzoic acid is volatile but below that at which phthalic acid is transformed into anhydride. In such a process steam or water may supplement the organic solvents.[66]

The fact that phthalic anhydride sells for about 18 cents a pound and U.S.P. benzoic acid for about 60 cents a pound makes the possibility of splitting out carbon dioxide from the dicarboxylic acid to form the monocarboxylic acid of interest from an industrial viewpoint. The loss in weight caused by the reaction is not great since theoretically 100 pounds of phthalic anhydride should yield 82.5 pounds of benzoic acid by this transformation.
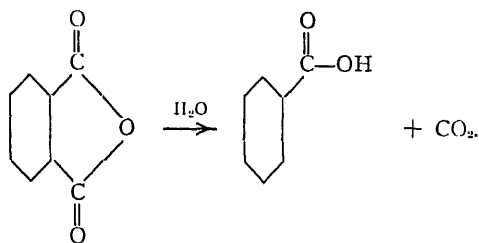
Hence, it is not surprising that a number of processes for accomplishing this transformation have been proposed, and that the transformation is being conducted on a large scale at the present time by a producer of phthalic anhydride, the Monsanto Chemical Co.

To make benzoic acid from phthalic acid or metal acid phthalates a mixture of the two phthalic compounds is heated in alkaline solution at temperatures varying from 150° to 300° C. Thus, a mixture of 500 pounds of 8.4 per cent sodium hydroxide solution, 296 pounds of phthalic anhydride, and 3 pounds of copper sulfate is heated in an autoclave at 200° to 220° C. for a period of about 5 hours. After making alkaline by further addition of sodium hydroxide, the cooled mixture is filtered and the benzoic acid precipitated by acidification with sulfuric acid. The benzoic acid is filtered off and may be purified by sublimation or distillation.[67]

The reaction may be affected in the solid phase by passing a mixture of calcium phthalate and calcium hydroxide through a narrow heated tube

[64] U. S. Pat. 1,685,634 (1928) Jaeger assr. to Selden Co.
[65] U. S. Pat. 1,686,913 (1928) Jaeger assr. to Selden Co.
[66] U. S. Pat. 1,694,124 (1928) Jaeger assr. to Selden Co.
[67] U. S. Pat. 1,712,753 (1929) Daudt to E. I. duPont de Nemours & Co., Inc.

by a screw conveyer.[68] The decomposition of the calcium phthalate results in the formation of benzoic acid salts which may be recovered from the product. Close temperature control of the narrow tube makes it possible to prevent undesirable side reactions or decompositions.

A number of vapor phase processes employing decarboxylating or carbon dioxide splitting catalysts have been proposed. In these processes the mixture of steam and phthalic anhydride vapor is circulated over the catalysts in a chamber maintained at temperatures varying from 300° to 450° C., depending on the active materials employed.

Among the simple catalysts that have been proposed oxides of zinc,[69] cadmium, lead, bismuth, silicon, aluminum, titanium may be mentioned.[70] Alkaline materials as sodium or calcium carbonates have also been claimed. The zinc oxide catalyst is prepared by spraying a solution of zinc nitrate, alone or with nitrates of other metals, on pumice and then heating the product in air. In practice the phthalic anhydride is simply steam distilled into the reaction chamber and the products separated by fractional condensation or selective solution.

Complex zeolites or base-exchanging compounds such as have been proposed as catalysts for the oxidation of naphthalene may also be used for this decarboxylating reaction.[71]

Benzoic acid prepared catalytically from phthalic anhydride may contain certain undesirable compounds, tars, and coloring materials and must of necessity be purified in some cases to obtain a marketable product. Naphthoquinone impurities are reduced to naphthohydroquinones by treatment of the product with sulfur dioxide or sodium bisulfite at 40° to 50° C. for 3 to 4 hours. Any phthalic anhydride remaining is converted to phthalic acid at the same time. Leaching with water is used to remove the reduced impurities.[72] Unconverted phthalic acid may also be separated from benzoic by treatment of the mass with sodium carbonate so as to convert the polycarboxylic acid into a primary salt while leaving the monocarboxylic acid unreacted. Solvent leaching is then used to separate the salt from the acid.[73] Colored impurities in benzoates from synthetic benzoic acid may be removed by oxidation with potassium permanganate.[74]

The price of $1.25 to $1.40 a pound for chloride free benzaldehyde makes it even more desirable to conduct the decarboxylating process under reducing conditions in order to reduce the benzoic acid to benzaldehyde at the time of its transformation. Proposals have been made to accomplish this end by passing the phthalic anhydride in the presence of reducing gases or vapors as hydrogen, methane, methanol, etc., over hydrogenating catalysts as chromium, iron, copper, manganese, cobalt or their oxides, possibly activated by additions of lead, beryllium, cerium, uranium, zinc

[68] U. S. Pat. 1,727,102 (1929) Fairweather, Beckatt, and Thomas assrs. to Selden Co.
[69] U. S. Pat. 1,645,180 (1927) Conover.
[70] Brit. Pat. 262,101 (1925) I.G. Farbenind.
[71] Brit. Pats. 309,024 (1928), 314,035 (1928); U. S. Pat. 1,714,956 (1929) Jaeger to Selden Co.
[72] Brit. Pat. 307,343 (1928) I.G. Farbenind.
[73] U. S. Pat. 1,770,393 (1929) Daniels assr. to Selden Co.
[74] U. S. Pat. 1,692,927 (1928) Calcott and Daudt assrs. to E. I. duPont de Nemours & Co., Inc.

or their oxides.[75] The multiple component zeolitic catalysts are useful since a combination of properties, hydrogenating and decarboxylating, may be obtained by the proper combination of elements.

$$\underset{\text{C—OH}}{\overset{\overset{\displaystyle O}{\|}}{\bigcirc}} \xrightarrow{\text{H}_2} \underset{\text{CH}}{\overset{\overset{\displaystyle O}{\|}}{\bigcirc}} + \text{H}_2\text{O}$$
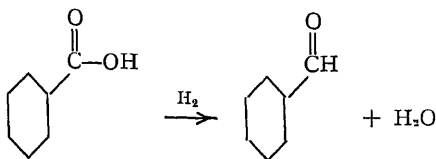
The claimed yields of benzoic acid are high as may be seen from the data contained in the patent literature.[76] A catalyst as simple as that consisting of sodium chloride coated on quartz fragments permits a conversion of 75 to 90 per cent of phthalic anhydride to benzoic acid at 360° to 420° C. Passage of phthalic anhydride vapors and hydrogen in the ratio of 2.95 kilos of anhydride per 6.75 cubic meters of hydrogen over a supported zinc oxide catalyst at 380° to 400° C. results in a conversion of 65 to 75 per cent to benzoic acid. Reduction to benzaldehyde and benzol also occur when 80 to 94 per cent of the anhydride are reacted per pass and the resulting benzoic acid is, hence, contaminated with these compounds. Iron oxide catalysts under similar conditions allow comparable conversions with only traces of aldehyde formed. Other catalysts, principally oxides, give similar yields and conversions. Converters of aluminum or copper are used. The exhaust gases contain large proportions of carbon monoxide with but small amounts of carbon dioxide showing that the water gas reaction occurs or that the anhydride is directly reduced.

Miscellaneous reactions. By passing dry ammonia over heated phthalic anhydride phthalimide $(C_6H_4\underset{\text{CO}}{\overset{\text{CO}}{\diagup\!\!\diagdown}}NH)$ is formed. This is essentially a vapor phase reaction occurring at temperatures above 100° C. Processes have been proposed for producing phthalimides directly by inducing reaction between naphthalene, oxygen, and a primary amine such as ammonia. The reaction is conducted in the vapor phase and in the presence of such catalysts as are ordinarily used for the vapor phase oxidation of naphthalene, i.e., vanadium or molybdenum oxides or mixtures. A stepwise process in which ammonia is added to the reaction products from naphthalene oxidation may be used.[77]

The oxidation of α-nitronaphthalene may be used to accomplish the same end.[78] Hot air is passed over the nitronaphthalene which is kept at a temperature of 130° to 170° C. to vaporize it and the mixture passed over pumice impregnated with molybdenum oxide or vanadium oxide

[75] Brit. Pat. 290,319 (1927) I.G. Farbenind.
[76] U. S. Pat. 1,714,956 (1929) Jaeger assr. to Selden Co.
[77] U. S. Pat. 1,450,678 (1920) Gibbs assr. to E. I. duPont de Nemours & Co., Inc.
[78] Brit. Pat. 183,044 (1921); U. S. Pat. 1,488,239 (1924) Green and Green assrs. to British Dyestuffs Corpn.

maintained at a temperature of 300° to 400° C. An excess of air, at least ten times that theoretically required, is essential. Pumice containing from 15 to 25 per cent of vanadium oxides gives a catalyst that becomes active at 300° C. and is best in a working range of 330° to 370° C. Molybdenum oxide catalysts require higher temperatures for activation and are, hence, not as satisfactory. A 40 to 50 per cent yield of phthalimide and a 15 to 20 per cent yield of phthalic anhydride is obtained. Since phthalic anhydride is the more volatile of these two products they are easily separated by distillation or sublimation. Fractional condensation of the product affords a practical method of separation since the phthalimide crystallizes out first and then the phthalic anhydride at a point considerably removed. Liquid phase oxidations of nitronaphthalene by sulfuric acid conducted in the presence of iron result in the formation of phthalic anhydride only since the ammonia is lost by volatilization.[79] Nitrophthalic acid, however, results from the chromic acid oxidation of α-nitronaphthalene.[80]

The alkyl naphthalenes, such as methyl naphthalene, may be oxidized to phthalic anhydride in the same manner as naphthalene, thus making it possible to use cruder grades of naphthalene. Thus, crude naphthalene obtained by centrifuging the oils from the proper cut from the distillation of coal-tar (whizzed naphthalene) consisting principally of naphthalene to the extent of 50 to 80 per cent and usually containing considerable quantities of alkyl naphthalenes and other ring compounds may be treated in a manner similar to that used in the oxidation of pure naphthalene. The reaction products contain phthalic anhydride, benzoic acid, naphthoic acids and anhydrides, etc.[81]

A striking illustration of the relative stability of the benzenoid and of a hydroaromatic ring is afforded by the oxidation of tetra-hydronaphthalene with air. The preponderating product is phthalic anhydride, with little or no tetrahydronaphthalic acid present, showing the selectively complete destruction of the non-benzenoid ring. Data on the oxidation of tetrahydronaphthalene are available from the work of Maxted,[27] and are shown in Table XLI.

TABLE XLI.—*Oxidation of Tetrahydronaphthalene with Air.*

Space velocity = 500 for both primary and secondary air
Carburetor Temp. = 100° C. (primary air)
Catalyst, tin vanadate unsupported

Catalyst Temp. ° C.	Yield Phthalic Anhydride Per Cent	Space Time Yields
280	52.8	0.025
290	41.7	0.020
300	31.7	0.015
310	10.6	0.005

[79] U. S. Pat. 1,443,094 (1919) Sasa.
[80] Beilstein and Kurbatov, *Ann.* 202, 218 (1880).
[81] U. S. Pat. 1,591,619 (1926) Gibbs to E. I. duPont de Nemours & Co., Inc.
[27] Maxted, *J. Soc. Chem. Ind.* 47, 101-5T (1928).

The fact that both space time and per cent yields of phthalic anhydride show decreases with temperature increases above 280° C. shows that the lowest temperature for efficient operation was not found. The abnormally low temperature at which the tin vanadate catalyst becomes active should make it applicable to the oxidation of a number of substances that ordinarily would decompose at the temperatures that are required for the activation of most of the oxidation catalysts.

Chapter XIV

Oxidation of Anthracene and Miscellaneous Polynuclear Compounds

Oxidation of Anthracene

At the beginning of the vat dye industry in the United States, before the vapor phase oxidation of naphthalene to phthalic anhydride had been perfected, producers of anthraquinone used anthracene as the raw material in a liquid phase dichromate oxidation process. However, the subsequent rapid development of the phthalic anhydride process, and the perfection of methods for producing cheap aluminum chloride of high quality has made it possible to manufacture synthetic anthraquinone at a price too low for the older oxidation method to meet.* However, the improved methods of vapor phase oxidation with the possibility of using partly purified anthracene have to some extent reduced the cost of the direct production of anthraquinone. Nevertheless, under present conditions, the direct oxidation processes cannot compete with the synthetic process. It should not be overlooked that the economics of the situation are complicated and that changed conditions in the industry could conceivably reverse the positions of the two methods. The problem of handling hydrochloric acid gas which is evolved in the synthesis, the cost of aluminum chloride and losses of benzene operate as disadvantages to the synthetic process, and although not of a decidedly serious nature, will still be factors for consideration in the competition.

The wide market for phthalic anhydride resulting in a large tonnage production has made possible a low price which may become lower as costs are reduced by an expanded production. This fact has an important bearing on the production of synthetic anthraquinone. Furthermore, the advent of cheap aluminum chloride has had its share in furthering the success of the process. Another factor favoring the synthetic product is the fact that it is of a high quality, comparable to that obtained from the catalytic oxidation after supplementary purification. Thus, the synthetic material produces dyes of a brilliance not possible by the use of the oxidation product without further purification. An important point in the present superiority of the synthetic material is that although oxidation of anthracene yields only anthraquinone, the synthetic process involving

* *See* Chapter XIII.

phthalic anhydride can be made to yield the chloro-, methyl-, amino-, etc., derivatives of anthraquinone very simply.

No yield or purity advantages accrue from the use of very pure anthracene in the vapor phase oxidation process.* However, even the use of partly purified anthracene is too costly a process to compete under present conditions. The economic advantage in the use of a partly purified raw material is largely offset in the decreased production rate of a catalytic converter. The production rate is limited by the heat-removing capacity of the apparatus and is of controlling importance because it involves such vital factors as labor, power, and overhead charges. Although the theoretical heat evolution in the case of anthracene oxidation to anthraquinone is much lower than in the case of naphthalene to phthalic anhydride, the necessity for the complete combustion of impurities present in the partly purified material makes the actual heat evolution per unit of time very high even in the case of anthraquinone production.

In summary, it may be said that the present superiority of the synthetic anthraquinone process is an excellent example of the controlling importance of economic considerations in the selection of a proper technical method for the production of a commercial article.

Production of anthracene. The most important source of anthracene is coal-tar. In the distillation of coal-tar crudes the fractions coming off in the temperature ranges between 270° to 290° C. and 380° to 400° C. and known variously as "anthracene oil," "heavy oil," "dead oil," or "green oil" contains practically all of the anthracene present in the original crude tar. From this fraction 6 to 10 per cent is recovered as crude anthracene by allowing the solids to separate from the heavy oil, filtering, centrifuging, and hot and cold pressing.[1] In this way, the solids are freed from as much creosote as possible. Artificial cooling results in a more rapid and complete separation of the solid matter in the original oily fraction. The anthracene content of this solid mixture varies from 15 to 30 per cent, depending on the source of tar and the character of the purifying operation. Subsequent washing with crude solvent naphtha or light creosote oil gives a product containing from 30 to 50 per cent anthracene. This solvent naphtha wash removes the major part of the phenanthrene and the remaining product is less than one-half carbazole. Recovery of the anthracene in the state of purity essential to anthraquinone manufacture from this press cake mixture has been difficult and costly.[2] The European process of purification, which consists essentially in recrystallization from pyridine, was found to be suitable for the American crudes but the relatively high cost of pyridine was a barrier. Prior to the development of synthetic anthraquinone from phthalic anhydride, the pyridine process was used successfully with American crudes but the large demand for pyridine as an alcohol denaturant made its cost for this process inordinately high.

* J. M. Weiss, personal communication.
[1] *See* Brit. Pat. 255,429 (1925) Meiro for various modifications.
[2] *See* Spielmann, "The Constituents of Coal Tar," London, Longmans Green Co., Ltd., 1924.

Present costs of pyridine are but a fraction of that during the time of this development.

It is obvious from the similarity of the vapor pressures of these three compounds, phenanthrene, carbazole, and anthracene, that it is practically impossible to separate them completely by any process of distillation. That a considerable degree of separation may be effected, however, by volatilization in a stream of air followed by fractional condensation in a series of chambers has been shown by Gibbs.[3] By blowing air or flue gas laden with the vapors of anthracene press cake through orifices the materials can be made to deposit on the walls of screens or perforated metal plates in a large chamber. Loss of heat along the separating plates results in a temperature gradient from front to back of the chamber and permits a separation. Thus, with a press cake containing approximately 20 per cent anthracene, 25 per cent carbazole, 35 per cent phenanthrene and other hydrocarbons, and 20 per cent oil and water and vaporizing for the second time the material from the first collection chamber it was possible to obtain products containing 80 to 83 per cent carbazole from the first chamber, 75 per cent anthracene from the second chamber, and almost all phenanthrene from the third chamber. The yields obtainable by this process are rather low, however, and economically it cannot be operated to advantage.

FIG. 47.—Vapor pressures of anthraquinone and some of the constituents of coal tar.

1. Naphthalene
2. Acenaphthalene
3. Phenanthrene
4. Anthracene
5. Carbazole
6. Anthraquinone

Early methods of separation employed such solvents as oleic acid,[4] crude coal-tar solvent naphtha, light pyridine,[5] etc. Based on the selective solution of phenanthrene by the coal-tar naphtha, and of carbazole by the light pyridine, Clark proposed a complicated scheme for the separation and recovery of all three of these constituents. Recently, organic liquid compounds containing the furan nucleus have been found to have a highly selective solvent action on phenanthrene and carbazole.[6] Thus, furfural while dissolving phenanthrene and carbazole does not have a marked solvent action on anthracene at low temperatures. However, at elevated temperatures it does dissolve anthracene with the result that it is possible

[3] U. S. Pat. 1,456,848 (1921) Gibbs to the public.
[4] Ger. Pat. 38,417 (1886) Remy and Erhart *Chem. Zentr.* (3), 18, 396 (1887).
[5] Clark, *J. Ind. Eng. Chem.* 11, 204 (1919).
[6] a. Jaeger, *Ind. Eng. Chem.* 20, 1335 (1928); b. Brit. Pat. 304,179 (1928); Ger. Pat. 488,527 (1928); U. S. Pat. 1,693,713 (1929) Jaeger assr. to Selden Co.; c. French Pat. 667,178 (1929) Selden Co.; d. U. S. Pat. 1,764,031 (1930) Norton assr. to Selden Co.; e. U. S. Pat. 1,782,488 (1930) Thatcher.

to recrystallize anthracene from furfural quite readily. One crystallization has raised the anthracene content of the crude from 31 to 86 per cent with a 94 to 98 per cent recovery. Recrystallization permits recovery of 92-96 per cent quality anthracene with about 2 per cent carbazole present. Various other furan compounds such as methyl furfural, furfuryl alcohol, etc., have been tried and patented. By first using a solvent such o-dichlorobenzene it is possible to recover phenanthrene separately.

Carbon tetrachloride has also been claimed for the refining of anthracene.[6e] Finely divided crude anthracene is treated with the solvent in such proportions that oils and phenanthrene are dissolved. The remaining anthracene is then purified from carbazole in a subsequent operation.

Solvent or fractional condensation methods, however, do not give complete separation from the anthracene of such substances as acridine, fluoranthrene, fluorene, pyrene, methyl-anthracene, chrysene, acenaphthene, high molecular weight paraffin hydrocarbons, etc., which are present in the crude anthracene press cake. During the subsequent oxidation of anthracene by the liquid phase method these substances result in the formation of impurities difficult to separate from the anthraquinone and detracting considerably from its quality as a dye intermediate.

If recovery of the carbazole is not desired it may be quite readily removed from the anthracene-phenanthrene portion of the crude by reaction with caustic alkali or potash. The crude anthracene may be dissolved in aliphatic or aromatic organic bases such as pyridine, quinoline or the bases obtained from coal-tar, an equivalent amount of potassium hydroxide to react with the carbazole added, and the purified anthracene separated by cooling and filtering.[7] Heating to 160° to 170° C. is used to insure complete solution of the materials and to increase the reaction of the alkali with the carbazole. Ordinarily, simple fusion with caustic has been found to be sufficiently effective to remove the carbazole. Carbazole forms a non-volatile derivative:
$$\begin{array}{c} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!\!\Big\rangle N\,Na(K),$$
from which the other constituents may be removed by distillation. This method of carbazole removal, while thorough, is expensive and inapplicable except for small scale operation. The carbazole may be recovered from the alkali metal compound by hydrolysis with water for use in the synthesis of certain dyes.[8]

Recently, a process has been proposed for the purification of anthracene by the selective vapor phase oxidation of the impurities present.[9]

[7] a. Brit. Pat. 319,762 (1928) Rutgerswerke A.G. and Kahl; b. French Pat. 681,425 (1929) Kahl and Rutgerswerke, A.-G.
[8] See a. Houben and Fischer, "Das Anthracen und die Anthrachinone," Leipzig, Thieme, 1929, for further details regarding polynuclear compounds; b. Barnett, "Anthracene and Anthraquinone," New York, D. Van Nostrand Co., Inc., 1921.
[9] Jaeger, Ind. Eng. Chem. 20, 1330-35 (1928); Int'l Conf. Bit. Coal (1928), Pittsburgh, pp. 614-632, Carnegie Inst. Tech.; Chem. Trade J. 84, 325 (1929); Gas. J., January 29 (1930); Talbot and Watson, Ind. Eng. Chem. 21, 8 (1929).

Crude anthracene, which may contain as low as 12 to 15 per cent of anthracene, is vaporized with air and passed over catalysts favoring combustion of the heterocyclic and aliphatic compounds under such conditions that the anthracene is not attacked. Catalysts may consist of the oxides of titanium, iron, cobalt, vanadium, or vanadates of manganese, iron, cobalt, nickel, etc., mixed or separate and "stabilized" or reduced in activity by the addition of alkali salts or hydroxides. Multiple component base exchange compounds, as zeolites, have also been shown to be applicable to the process. The recommended catalyst is obtained from a mixture of 8.7 parts ferric oxide and 8 parts of titanium precipitated from solution by means of alkali. To this mixture suspended in 100 parts of water 14.2 parts by volume of $0.1N$ potassium hydroxide solution is added and the mixture taken up by 200 to 250 parts by volume of pea-sized pumice particles and the whole mass dried at 400° to 500° C. Temperatures of from 360° to 440° C. are used, depending upon the catalyst. In general, the higher the temperature to which the reacting mixture is exposed, the more completely the impurities are destroyed. Losses of anthracene become serious, however, at the higher temperatures. A high-grade anthracene may be obtained that contains varying amounts of phenanthrene, impossible to remove by oxidation without simultaneous destruction of anthracene. This product may be oxidized directly or the phenanthrene may be removed by suitable solvents such as crude coal-tar solvent naphtha,[5] furfural,[6] etc. Preliminary treatment with pyridine may be used prior to oxidation if the carbazole is to be recovered.

With a crude containing 25 to 35 per cent anthracene, air ratios of 1 part of crude to 15 to 40 parts of air by weight are used, preferably 1 to 25 for most of the catalysts tried. Converters made up of a large number of tubes 1 to 3 cm. in diameter which contain the catalyst and are surrounded with a liquid bath to maintain the temperature and remove heat are used for the process. Both the high air ratios and the type of converters used serve to maintain the temperature at a uniform value and to prevent losses of raw material by over oxidation.

Jaeger[9] has claimed that when semi-purified anthracene is used as the starting material, it is not necessary to recover the purified anthracene since it is possible to produce a chemically pure anthraquinone with 90 per cent yields by combining the purification with the final oxidation stage. Successive sets of catalyst in the same converter or separate converters directly in series may be used.

It is questionable, however, whether this process can be economically applied on a commercial scale at the present time in competition with cheap anthraquinone produced from phthalic anhydride.

The net result of the process is that impure or partly purified anthracene may be oxidized directly to anthraquinone. From the standpoint of equipment cost it does not matter whether two single catalytic converters

each burn impurities and oxidize anthracene to anthraquinone or whether one burns impurities and the next in series oxidizes anthracene. The limiting factor is removal of heat and the rate of production is limited by the rate of heat removal possible in the equipment. Even the great advantage that the use of impure anthracene has over the costly pure material is offset by the limited production capacity.

Liquid phase oxidation. In spite of the difficulties attending the purification of anthracene by the solvent extraction method, the first vat colors made in this country were from anthraquinone obtained by the oxidation of anthracene.[10] Anthracene crystallized from pyridine is distilled with superheated steam or sublimed to render it in a finely divided form suitable for oxidation. Oxidation with chromic acid is simple and almost quantitatively to anthraquinone. However, disposition of the chromic sulfate resulting from the process presents serious difficulties.[11]

Oxidation of anthracene with chromic acid in hot glacial acetic acid is quantitative and may be used for the analysis of anthracene.[12] On a commercial scale this method is too expensive and a cheaper process has been used. Substitution of sulfuric acid for acetic and dichromates for chromic acid lowered the costs sufficiently to make the process commercially applicable. Disposal of resulting chromic sulfate, however, represents a troublesome problem. In Germany it has been used in the leather industry and elsewhere attempts have been made to regenerate the chromic acid electrolytically, a process also attended with unavoidable difficulties. The crude anthraquinone resulting from the sulfuric acid oxidation is dissolved in hot concentrated sulfuric, reprecipitated by dilution, filtered off, and sublimed or recrystallized from a suitable solvent.

Numerous other methods have been proposed to take the place of the sulfuric acid method of oxidation. Excellent results have been claimed from the use of sodium nitrate or chlorate in the presence of a large excess of magnesium chloride.[13] Sodium hypochlorite solutions containing traces (0.01 gram per 200 cc.) of osmium salts are active oxidizing agents at ordinary temperatures.[14] A number of processes using nitric acid, oxides of nitrogen, or nitrites as catalysts have been proposed for the oxidation with oxygen in liquid phase.[15] The use of nitric acid or nitrogen oxides has the defect that impurities are formed which are difficult to remove in the subsequent purification of the product. By passing a mixture of nitrogen dioxide and air over powdered anthracene at 200° C. good yields of anthraquinone are obtained.[16] The anthracene may be intimately mixed

[10] Bishop and Sachs, *Ind. Eng. Chem.* 18, 1331-4 (1926).
[11] Klipstein, *Ind. Eng. Chem.* 18, 1327-29 (1926).
[12] Kopp, *Moni. sci.* (3) 8, 1159 (1918).
[13] Hofmann, Quoos, and Schneider, *Ber.* 47, 1991 (1914); Ger. Pat. 277,733 (1913).
[14] a. Hofmann and Ritter, *Ber.* 47, 2238 (1914); *see also* b. Hofmann, *Ber.* 45, 3329-36 (1912); *ibid.* 46, 1657-68 (1913); *ibid.* 48, 1585-93 (1925); Brit. Pat. 20,593 (1913).
[15] a. Brit. Pats. 156,215 (1921); 156,538 (1921); 156,540 (1921); 169,145 (1921). Chem. Fabriken Worms Akt.-Ges.; b. U. S. Pats. 1,466,683 (1923); 1,467,258 (1923) Ullrich.
[16] Brit. Pat. 16,312 (1910) Wetter.

with pumice, asbestos powder, or similar inert support. This practice is claimed to result in a lessened contamination of product with nitrogen compounds.[17] The reaction for using nitrogen oxides in the presence of compounds of zinc or copper oxides for preparing aromatic nitro-compounds is described in the parent patent and is used also for oxidizing anthracene to anthraquinone. A reaction mechanism involving the inter-. mediate formation of a meso-nitro-dihydro-anthranol is postulated as in the case where anthracene is treated with nitrous gases in acetic acid solution, and nitrogen later eliminated during the reaction. To avoid .the difficulties resulting from the removal of the small but persistent amounts of nitrated products that remained in the anthraquinone, the anthracene was first mixed with zinc dust, lead oxide, or other substances to react with the nitric acid formed. In this way the formation of a pure product in almost theoretical yield was claimed.[18]

Electrolytic oxidation of anthracene in 20 per cent sulfuric acid solution with 1 per cent of vanadium pentoxide present is carried out at 80° C. with lead electrodes and a current density of 300 amperes per square meter at 1.6 volts. Good yields have been claimed [19] for this process. Air under pressure has been used for the oxidation of anthracene in the form of dispersions in aqueous ferric sulfate solutions,[20] or as a solution in pyridine or dispersion in aqueous alkaline solutions preferably in the presence of catalysts [21] of copper, cobalt, nickel or lead compounds. Vanadium compounds have been found more active than chromium compounds for use as oxidation catalysts in the form of suspensions in the liquid phase, as in the preparation of aniline black.[22] Anthracene suspended in water or dilute sulfuric acid or dissolved in a solvent as acetone is oxidized with ozone, or ozonized oxygen at ordinary temperatures.[23]

Andrews has suggested the oxidation of anthracene by means of boiling sulfuric acid and oxidizing agents as sodium chromate, manganese dioxide, etc., in the presence of catalysts such as oxides of molybdenum, vanadium or mixtures in a state of fine subdivision.[24]

The use of mild oxidizing agents or operation under mild conditions usually results in products other than anthraquinone from the oxidation of anthracene. Thus, oxidation with tin oxide, manganese oxide, cerium acetate, or vanadium pentoxide in glacial acetic acid results in the formation of a mixture of acetates.[25a, b]

[17] Ger. Pats. 215,335 (1908) (addn. to Ger. Pat. 207,170 (1908)); 234,289 (1908); 254,710 (1910) (addn. to Ger. Pat. 234,289) Chem. Fabrik Gruenan, Landshoff und Mayer Akt.-Ges.
[18] Ger. Pats. 256,623 (1911); 292,681 (1914) Farbwerke v. Meister Lucius u. Brüning.
[19] Brit. Pat. 19.178 (1902); French Pat. 345,701 (1904); U. S. Pat. 823,435 (1906). *Compare* Creighton and Fink. "Principles and Applications of Electrochemistry," New York, John Wiley & Sons. Inc., 1924, Vol. I, pp. 548-9.
[20] Brit. Pat. 8431 (1887) Poirrier and Rosenstiehl.
[21] Ger. Pat. 292,681 (1914).
[22] Witz, *Compt. rend.* 83, 348-50 (1876); *ibid.* 87, 1087-8 (1878); *Bull. soc. ind. Mulhouse* 1876, p. 425; *Dingler's polytech. J.* 224, 639-42 (1877).
[23] Brit. Pat. 5514 (1915) Heinemann.
[24] U. S. Pat. 1,324,715 (1919) Andrews assr. to Selden Co.
[25] a. Meyer, *Ann.* 379, 73 (1911); b. Schulze, *Ber.* 18, 3036 (1885).

Anthracene ⟶ [chemical structure diagram] ⟶ [chemical structure diagram]
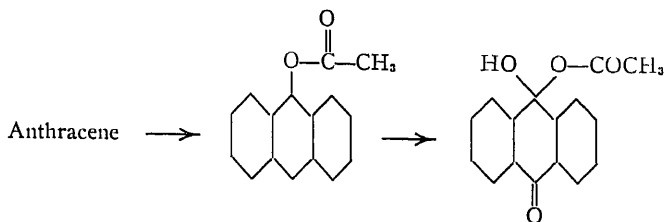
Even the action of nitric acid on anthracene in hot glacial acetic acid has been found to result in formation of dihydrodianthron.[25c, d]

Vapor phase oxidation. The first claims to be made public for the vapor phase oxidation of anthracene to anthraquinone appeared in a patent issued to Walter.[26] As catalysts, the oxides of the metals of the fifth and sixth groups of the periodic system were used. The oxidation of various substances in the vapor phase was claimed but the importance of the new process was not recognized until the war caused a revival in interest. Although the original process was not directly applicable to large scale production because of limitations in catalyst activity, temperature control, and heat removal, it did furnish a basis for the subsequent development of the general vapor phase oxidation processes.

Application of the same methods to the oxidation of anthracene in the vapor phase as had been found to give good results in the oxidation of naphthalene to phthalic anhydride resulted in the formation of anthraquinone in good yields. In the early process anthracene was vaporized, mixed with an excess of air over that necessary for the desired oxidation, and the resulting mixture forced over catalysts supported on trays or on a porous material by baffles suitably located in the reaction chamber. Catalysts consisting of the oxides of metals of the sixth group of the periodic system, viz: chromium, molybdenum, tungsten and uranium, were found to be effective at temperatures ranging from 250° to 650° C., preferably 500° C.[27]

Although the earlier workers undoubtedly felt that a somewhat milder form of catalyst than had been used in the oxidation of naphthalene to produce phthalic anhydride would be necessary for the formation of anthraquinone, it was soon shown that vanadium catalysts were applicable. These catalysts consisting of vanadium oxides supported on pumice were used in tubular reaction chamber.[28] Such disposition of the catalyst represented an advance over the early method since it permitted a better control of gas rates and time of contact, a necessity when such active catalysts were used for the small degree of oxidation required in the reaction. A temperature range of 300° to 500° C. was specified and the use of diluent gases to control the reaction intimated.

[25] c. Dimroth, *Ber.* **34**, 219 (1901); d. Scholl and Mansfeld, *Ber.* **43**, 1736 (1910).
[26] Ger. Pat. 168,291 (appl. 1904), (pub. 1906) Walter; *Chem. Zentr.* 1906, 1199.
[27] U. S. Pat. 1,303,168 (1919) Conover and Gibbs assrs. to the public.
[28] U. S. Pat. 1,355,098 (1920) Weiss and Downs assrs. to the Barrett Co.

A number of other catalysts, combinations, and variations of the basic process have been proposed. Simple vanadium pentoxide catalysts, such as were proposed by Walter and used by the early workers, did not prove to be applicable to the production of pure anthraquinone in high yields even when highly purified anthracene was used. Various modifications have been proposed. The vanadium oxide catalysts may be mixed with or combined with other substances such as metallic oxides, asbestos, pumice, etc.,[29] or with another catalytically active material such as molybdenum oxide to alter its activity.[30] Zeolitic materials containing combined vanadium may be used.[31] The metal salts of acids from elements having more than one degree of oxidation, e.g., vanadates, chromates, molybdates, uranates, stannates, and arsenates of copper, silver, lead, thorium, cerium, nickel, and cobalt greatly reduce the temperature ordinarily required for the oxidation when simple oxide catalysts are used.[32] For example, a catalyst prepared by dissolving one mol of vanadic acid in a solution containing 6 mols of alkali, precipitating with 3 mols of copper sulfate, filtering, washing, and distributing on fifty times the weight of pumice particles is capable of oxidizing anthracene in the presence of air without loss at a temperature of 180 to 190° C.

Catalysts such as titanium oxide supported on pumice require activation to function properly. By adding about 2 per cent by volume of nitrogen oxides to a mixture of anthracene vapor containing a four-fold excess of air over that theoretically required oxidation occurs smoothly over titanium oxide at 400° to 500° C.[33]

When mixtures of anthracene and phenanthrene, such as are obtained by removing carbazole from anthracene press cake by caustic fusion, are oxidized, mixtures of phthalic anhydride and anthraquinone result.[34] A separation of these valuable products is effected by washing out the acids with an alkali solution and recovering as sodium salts or as acids by acidification subsequent to removal of anthraquinone by filtration. The products may be distilled or sublimed to separate from any unoxidized material that may be present. Maleic acid may also be present in the products to a small extent and is recovered with the phthalic anhydride from which it must be removed as an impurity.[35]

As indicated by available data the major product obtained in the catalytic vapor phase oxidation of anthracene aside from total combustion products obtained in some cases, is anthraquinone. Operating conditions are designed and controlled in such a way that this is the main product, obtained in as pure a form as possible.

[29] U. S. Pat. 1,417,367 (1922) Conover and Gibbs assrs. to the public.
[30] U. S. Pat. 1,636,856 (1927) Craver.
[31] U. S. Pats. 1,685,635 (1928); 1,786,950 (1930) Jaeger assr. to Selden Co.
[32] Brit. Pats. 156,244-5 (1920); U. S. Pat. 1,787,416 (1930) Wohl assr. to I. G. Farbenind.
[33] Brit. Pat. 182,843 (1922) Atack assr. to British Alizarine Co., Ltd.
[34] a. U. S. Pat. 1,444,068 (1922) Gibbs assr. to E. I. duPont de Nemours & Co., Inc.; b. Downs, *J. Soc. Chem. Ind.* 46T, 383-6 (1927).
[35] Note that under certain conditions as in fuming sulfuric acid anthraquinone forms phthalic

$$+ 3O \longrightarrow + H_2O.$$
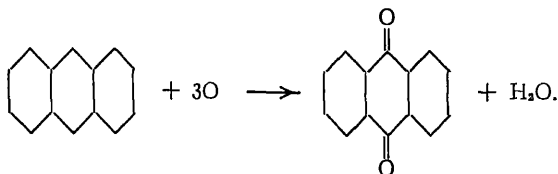
While the overall reaction of anthracene oxidation to form anthraquinone as shown above involves the interaction of three atoms of oxygen per molecule of hydrocarbon, the actual mechanism of the catalysis is more or less obscure. From the observations of Senseman and Nelson [36] the vanadium oxide catalysts function by being alternately reduced to a lower oxide by the hydrocarbon and oxidized to the pentoxide by the oxygen of the air used. Thus:

(1) Vanadium pentoxide + anthracene = anthraquinone + water + lower oxide of vanadium
(2) Lower oxide of vanadium + oxygen = vanadium pentoxide.

By placing anthracene and vanadium pentoxide in a tube, evacuating to a pressure of 2 mm. of mercury, and heating to 400° to 500° C. for 1 hour after sealing, these workers were able to show that 12 to 15 per cent of the anthracene had been oxidized to anthraquinone. This indicates that reaction (1) above will occur under proper conditions. The vanadium pentoxide changed in color from brown to bluish green during the procedure, indicating the presence of lower oxides. This bluish-green oxide could be readily oxidized to the pentoxide by heating in a stream of air at 400° to 500° C. showing that reaction (2) is valid under the conditions. In the oxidation of aromatic hydrocarbons nuclei to form useful organic oxygen derivatives only catalysts of metals having several degrees of oxidation and capable of ready reduction to a lower oxide and reoxidation to a superior oxide have been found effective in producing commercial yields. This is an added point toward the evidence that some such mechanism as alternate reduction and oxidation of the metal oxide catalysts is effective.

Further evidence from the results of these workers indicates that this alternate reduction and oxidation of the catalyst controls the rate of the overall reaction. The fact that alteration of the physical condition of the catalyst, such as surface exposed or fineness of subdivision, did not result in comparable alterations in the rate at which product was obtained shows that the rate at which the reactants reached the catalyst surface was not a controlling factor.

With vanadium pentoxide catalysts disposed in various ways in a glass tube 16 inches long and 1⅞ inches inside diameter and electrically heated Senseman and Nelson were able to obtain yields up to 81 per cent

[36] Senseman and Nelson, *Ind. Eng. Chem.* 15, 521-4 (1923).

of the theoretical with a product containing 99 per cent anthraquinone. The best results were obtained at a reaction temperature of 410° to 425° C., an air flow of 300 cc. per minute, and about 0.3 gram of anthracene per liter of air. This amount of air is not quite 3.5 times that theoretically required for the oxidation, and represents a lower ratio of air employed to that required than is used in the oxidation of naphthalene to phthalic anhydride. Compared with the 0.3 seconds used in present commercial practice, the times of contact used in this work were relatively long. In these experiments, when the reaction temperature dropped to 350° to 360° C., the reaction product contained some red material and much charred or tarry matter together with considerable unchanged anthracene. However, when the indicated temperature rose to over 25° or 30° C. above 400° C. the yield of anthraquinone dropped off due to complete combustion, although the product was obtained in a purer form at the higher temperatures.

Anthraquinone from the chromic acid oxidation process or the vapor phase oxidation process is purified by sublimation. Ordinarily, the temperature used for the sublimation varies from 200° to 350° C. and may become higher because of localized overheating. The temperature must be closely controlled since anthraquinone begins to decompose appreciably at about 450° C. and slightly at even lower temperatures.[37] The rate of decomposition is not materially affected by the presence of air, water vapor, or oxygen and the products are generally poorer in oxygen than the original. These impurities are soluble in alkalis to give colored solutions.[38]

Heat of reaction. Since only 3 atoms of oxygen react with each mol of anthracene in forming anthraquinone the heat given up by this reaction is considerably less than in the case of the oxidation of naphthalene to phthalic anhydride where 9 atoms of oxygen react per mol of hydrocarbon. From the heats of combustion of anthracene and anthraquinone [39] the heat of the reaction may be calculated. In this case 1348 B.t.u. are evolved per pound of anthraquinone formed. If total combustion is prevented to a large extent by keeping the temperature of reaction low, then the heat that must be removed from the reactor while still large, if rapid rates are used, does not present the problem that it does in the case of naphthalene oxidation. The complete combustion of impurities present in impure anthracene and the complete combustion of a portion of the anthracene itself necessarily increases the amount of heat evolved in commercial operation above the theoretical value. Therefore, similar apparatus is used and the heat removed from the large number of small catalyst tubes by means of a liquid bath which also acts as a means for temperature control.[40]

[37] Lewis and Schaffer, *Ind. Eng. Chem.* 16, 717 (1924).
[38] For the determination of anthraquinone in mixtures of aromatic hydrocarbons *see* Nelson and Senseman, *Ind. Eng. Chem.* 14, 956 (1922); *ibid.* 16, 1185 (1924).
[39] Kharasch, "Heats of Combustion of Organic Compounds," *Bur. Standards J. Research*, February, 1929.
[40] U. S. Pat. 1,614,185 (1927) Canon and Andrews.

Oxidation of Miscellaneous Polynuclear Compounds

Phenanthrene. Phenanthrene is isomeric with anthracene and is obtained from anthracene press cake by use of selective solvents after carbazole removal by caustic fusion and distillation. It may be oxidized to phenanthraquinone, which is used in the preparation of dye stuffs, and phthalic anhydride in the same processes used for the other aromatic hydrocarbons.[41] Phthalic anhydride is the main product and unless conditions are very carefully controlled phenanthraquinone forms in only small amounts.[42]

phenanthrene + 18O → phthalic anhydride + $6CO_2$ + $3H_2O$.
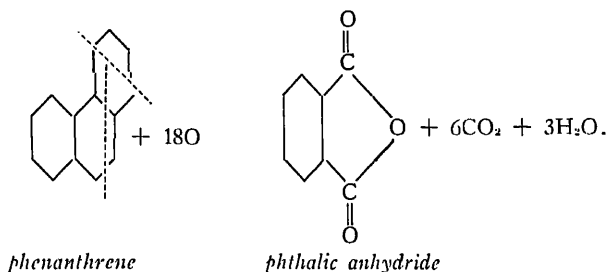
The presence of benzoic acid or of diphenic acid, formed in the wet oxidation of phenanthraquinone, has not been reported in the products of phenanthrene oxidation in the vapor phase. A naphthalic acid has been found and the presence of quinones established in the products.[41b] Mechanism for this oxidation cannot be postulated because of the present lack of data.

On oxidation with chromic acid phenanthrene yields first phenanthraquinone, and then diphenic acid,

HOOC   COOH
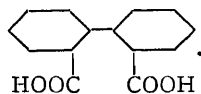
Phenanthraquinone, $\begin{array}{c} C_6H_4-CO \\ | \quad\quad | \\ C_6H_4-CO \end{array}$, melts at 200° C., boils without decomposition at 360° C., and is non-volatile with steam. Its diketonic character enables it to yield di-derivatives with sodium bisulfite and hydroxylamine.

Acenaphthene. The catalytic vapor phase oxidation of acenaphthene results in the formation of a variety of products such as: acenaphthylene, acenaphthoquinone, naphthaldehydic acid, naphthalic anhydride, maleic acid, etc.[43] Catalysts similar to those used in the oxidation of anthracene

[41] U. S. Pat. 1,288,431 (1918) Lewis and Gibbs.
[42] a. Downs, *J. Soc. Chem. Ind.* 46, 383-6T (1927); *see also* b. Fittig and Ostermayer, *Ann.* 166, 367 (1873); c. Fittig and Schnutz, *ibid.* 193, 116 (1878); d. Graebe and Aubin, *ibid.* 247, 263 (footnote) (1888); e. Anschütz and Schultz, *ibid.* 196, 50 (1879).
[43] a. U. S. Pat. 1,439,500 (1922) Bailey and Craver assrs. to Barrett Co.; b. U. S. Pat. 1,649,833 (1927) Lewis assr. to National Aniline and Chem. Co.; c. Brit. Pat. 318,617-8 (1928); French Pats. 680,100-680,541 (1929) Jaeger assr. to the Selden Co.

are used. With vanadium pentoxide catalysts, however, and acenaphthene-air mixtures in the ratio of 1 to 6.2 by weight a complex mixture of intermediately oxidized products is obtained at 400° C. The use of steam or diluent nitrogen may be used to control the reaction to give a product that may be separated by chemical means or fractional sublimation.

With a catalyst of manganese dioxide at a temperature of about 400° C.[48b] mixtures of air and acenaphthene containing 9 to 12 volumes of air in excess over that required for oxidation to acenaphthylene may be oxidized almost theoretically to acenaphthylene,
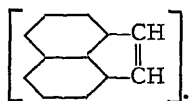
Under similar conditions but with temperatures of about 500° C., the product consists principally of naphthalic anhydride,
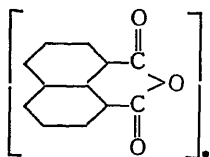
When acenaphthylene and naphthalic anhydride are produced together, separation may be effected by passing the vapors through a condenser maintained at a temperature of 100° to 200° C., at which temperature the anhydride condenses while the acenaphthylene and acenaphthene pass to a condenser at room temperature. Acenaphthylene may be separated from acenaphthene with sodium bisulfite.

Catalysts composed of the vanadates, vanadites, or molybdates of iron, silver, manganese, or aluminum are effective at temperatures of 350° to 420° C.[48c] Control of operating conditions or admixtures of steam in certain amounts permits the formation of certain of the products in preponderance.

Fluorene. Fluorene, diphenylene methane, $\begin{smallmatrix} C_6H_4 \\ | \\ C_6H_4 \end{smallmatrix} \Big\rangle CH_2$, is formed by passing the vapor of diphenyl methane through a red hot tube. It melts at 113° and boils at 295° C. Small amounts are found in coal-tar.

Oxidation with chromic acid converts it into diphenyl ketone, $\begin{smallmatrix} C_6H_4 \\ | \\ C_6H_4 \end{smallmatrix} \Big\rangle CO$. Oxidation with lead oxide at 310° to 330° yields di-diphenylene-ethylene:

$$\begin{smallmatrix} C_6H_4 \\ | \\ C_6H_4 \end{smallmatrix} \Big\rangle C = C \Big\langle \begin{smallmatrix} C_6H_4 \\ | \\ C_6H_4 \end{smallmatrix} .$$
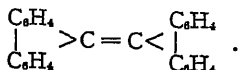
By oxidizing in the vapor phase with oxygen in the presence of suitable diluents as nitrogen or steam,[44] over certain catalysts the extent of oxidation may be controlled and the fluorene changed to fluorenone, diphenylketone, with good yields. Vanadium oxides or other compounds supported on inert carriers act as suitable catalyst for the reaction at temperatures in the range 300° to 700° C.

$$\begin{array}{c} C_nH_4 \\ | \\ C_nH_4 \end{array} > CH_2 + O_2 = \begin{array}{c} C_nH_4 \\ | \\ C_nH_4 \end{array} > CO + H_2O.$$
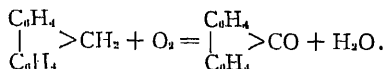
Salts of metal acids of elements in the fifth and sixth groups of the periodic system are also suitable catalysts.[45] The tubular type of reaction chambers as are used in other aromatic oxidation processes are applicable to the purpose.

Nitro-anthracene. Nitro-anthracene may be oxidized to nitroanthraquinone by passing the vapors mixed with air over catalysts such as tin vanadate at a temperature of 260° to 300° C.

[44] U. S. Pats. 1,374,695, 1,374,670 (1921) Weiss and Downs assrs. to Barret Co.
[45] U. S. 1,764,023 (1930) Jaeger assr. to Selden Co.

Chapter XV

Apparatus

The reactions involved in the direct vapor phase oxidation of organic compounds to oxygenated intermediate products are highly exothermic, and, other things equal, are extremely sensitive to temperature changes. Hence, in any process involving oxidation it is essential that adequate means be provided for the removal of heat and for the control of temperature, if other than complete oxidation products are to be obtained. This is especially true in the case of the oxidation of aromatic hydrocarbons to form intermediate products of oxidation, i.e., naphthalene to phthalic anhydride, toluene to benzaldehyde and benzoic acid, benzene to maleic anhydride, etc., where considerable oxidation of the molecule must occur in order for the desired product to result. Consequently the design of the catalytic apparatus for these reactions is of the utmost importance, and progress in this field of organic reactions has been marked largely by improvements in apparatus.

APPARATUS FOR THE OXIDATION OF AROMATIC HYDROCARBONS

Converter

The first industrial apparatus to be used in the vapor phase oxidation of naphthalene to phthalic anhydride depended upon air cooling for removal of heat and control of temperature. In such apparatus the catalyst was usually supported on metal trays which made thermal contact with the outside walls of the reactor tube. By such an arrangement a portion of the heat generated by the oxidation at the surface of the catalyst was conducted to the outside walls and there dissipated to the atmosphere by radiation or other means. By limiting the extent to which reaction occurred or by using large proportions of air or other gases it was possible to operate the process without excessive losses to complete combustion products. Cool air admitted at intervals along the length of the reaction vessel was used to prevent the temperature from rising excessively.

That such an apparatus was not very satisfactory may be easily recognized from a consideration of the characteristics of the oxidation reaction. In oxidations such as that of naphthalene to phthalic anhydride there is a specific and rather narrow temperature range within which the best results are obtained. Depending upon what catalyst is used there is some

definite temperature at which oxidation is initiated for each of the intermediate compounds that are formed by the different steps of the oxidation, and there is a definite temperature range in which the desired product is relatively stable in the presence of unreacted oxygen, original hydrocarbon, and intermediate oxidation products. Above this temperature range unlimited oxidation may occur to too great an extent and high losses result. For the highest efficiency in conversion and yields to be realized it is, hence, necessary that the temperature be maintained at this desired range and that large quantities of heat be removed at this temperature.

The difficulties of the old type apparatus were in both the inability to remove large quantities of heat at a high temperature level and in the uneven temperatures both along and across the reactor. The injection of air or other cooling gas or vapor near the reaction zone resulted in both undesirable dilution, and too rapid and localized cooling.

Radiation had to be largely depended upon for the removal of heat as the heat of reaction is large compared even with the sensible heat of ten times the quantity of air theoretically required to oxidize naphthalene to phthalic anhydride, when the air-naphthalene mixture is preheated in a heat interchanger to about 350° C. prior to striking the catalyst. Also the larger the quantity of naphthalene completely burned because of poor temperature control, an event perfectly capable of occurrence due to the presence of excess air, the greater would be the amount of heat generated. This accumulative and accelerating effect readily and frequently resulted in explosions. The largest converter for phthalic anhydride production which employed cold air injection between catalyst shelves could produce about 50 pounds of product on days when operation was satisfactory.* In operation the air valves were manually controlled with minute to minute observations of the thermocouples. Mechanically controlled valves could probably be used to increase greatly the usefulness of this type of apparatus by automatic action, but the probable lag in injection of air after a temperature rise or in decrease of air after a temperature drop would lead to irregular temperature fluctuations and a contaminated product. Also large volumes of air or flue gas are objectionable from the standpoint of product recovery and have been discouraged as much as possible. The use of thermocouples placed at random in a catalyst mass for determining the catalyst temperature and controlling operation thereby is far from satisfactory. The couple indicates the temperature at only a certain point and depending on the location in the catalyst can either show a temperature far lower than may actually exist at some other point or may give entirely misleading data when showing the correct operating temperature since the greater mass of the catalyst might be at much too low a temperature. A multiplicity of couples would eliminate the disadvantage but the difficulty of placing them, checking their correctness, and in periodically reading them would act as a severe deterrent to such practice.

* J. M. Weiss, personal communication.

The type of apparatus pictured in Figure 48 represented considerable improvement. In this the catalyst was still supported on trays or on screens in layers about fifty times as long and broad as deep. Between each set of catalysts layers or reaction zones a cooling medium was circulated through a suitable set of tubes. In operation, the reacting gases and vapors were cooled by contact with these tubes between the catalyst zones and heat was removed from the catalyst trays by radiation. Proper control of the cooling medium permitted higher yields and better conversions to be realized.[1]

Another modification in which liquids could be used as a cooling medium is shown in Figures 49 and 50. In this apparatus the reacting mixture passed continuously through a catalyst layer without intermittent
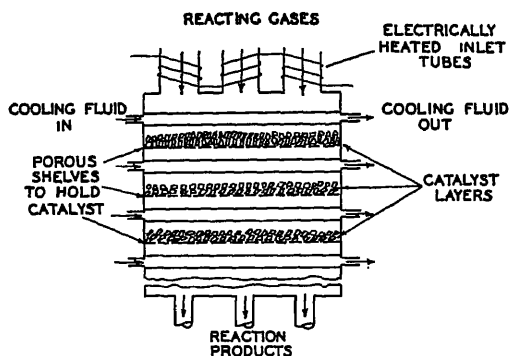
FIG. 48.—Early forms of catalytic oxidation apparatus. (Downs and Stupp.)

cooling. Heat of reaction was removed by a liquid cooling medium circulating in direct contact with the catalyst chamber.[2] Abrupt changes in the temperature of the reaction could thereby be avoided. However, with a cooling fluid such as water the sharp lowering of catalyst temperature at points immediately adjacent to the cooling chamber resulted in a lowered efficiency as far as utilization of catalyst was concerned. The normal temperature range for efficient operation of aromatic hydrocarbon oxidations is between 400° and 500° C. for vanadium pentoxide catalysts, and that portion of the catalyst cooled below this point is, of course, relatively ineffective, depending on the degree of cooling.

Figure 50 shows specifically the cross section of one of the units proposed in this patent and furnishes an excellent idea of the enormous volume of cooling medium compared with reaction space contemplated in the patent design. Because of the large cooling space the production based on apparatus volume and weight could only be relatively small. To increase the total productivity of a plant it was contemplated to use a

[1] U. S. Pats. 1,464,845 (1923); 1,515,299 (1924) Downs and Stupp assrs. to Barrett Co.
[2] U. S. Pat. 1,324,443 (1919) Conover.

number of these units placed on each other and connected as shown in Figure 49. The large outside surface of the apparatus was capable of radiating more heat than could be generated by the oxidation reaction
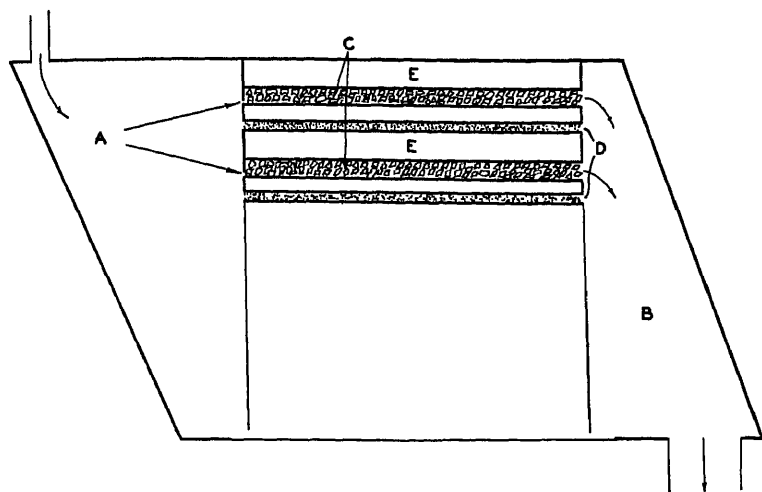
Fig. 49.—Catalytic oxidation apparatus with cooling fluid in contact with catalyst chambers.
A—Inlet Chamber
B—Exit Chamber
C—Catalyst Space
D—Insulation
E—Cooling Fluid

occurring in the restricted catalyst chamber, and it was, hence, necessary to supply heat to the "cooling" medium in order to maintain catalyst temperatures sufficiently high to permit reaction. The patent had apparently
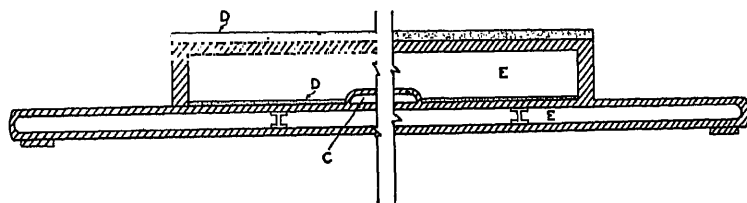
Fig. 50.—Cross section of apparatus shown in Fig. 49.
C—Catalyst Space
D—Insulation
E—Cooling Fluid

contemplated external cooling of as well as condensation of the vapors of the circulating fluid, and the process had not been worked out experimentally prior to designing and patenting. There is no evidence that it

has ever been used industrially, and consequently no data are available on its commercial operation. However, in experimental operation it has been found necessary to add external heat in quantities several times as great as that generated by the reaction in order for proper operating temperatures to be maintained.

Although this apparatus closely resembles the vertical tube mercury bath converter developed by Downs * in that it provided for liquids in thermal contact with the catalyst zone, it lacked certain features which

WATER OR STEAM

CONDENSER

WATER

AIR PLUS VAPOR TO BE TREATED

BOILING LIQUID

CATALYST MASS

TREATED VAPOR-AIR MIXTURE
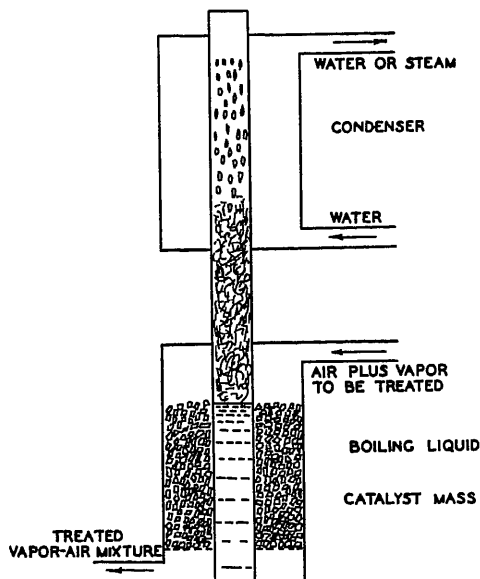
FIG. 51.—Apparatus for removal of reaction heat by boiling of a liquid.

would have made it successful. The apparatus seems specifically intended to limit the maximum temperature in the catalyst chamber without regard to the minimum temperature, which is of equal importance in insuring good production of a pure product, since it provided for a circulated and cooled liquid. It was not automatic and necessarily required a control of the degree of cooling (or heating) which the circulated liquid would require during operation.

By retaining the principle of liquid cooling but by substituting a more narrow catalyst zone and a liquid boiling at the reaction temperature for removal of heat, apparatus similar in principle to that shown by Figures 51 and 52 was developed. The use of small or flat catalyst tubes insured uniform temperature distribution across the catalyst zone,[3] by making it

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* *Cf.* p. 454.
[3] a. U. S. Pat. 1,614,185 (1927) reissue 16,824 (1927) Canon and Andrews assrs. to Selden Co.; b. Downs, *J. Soc. Chem. Ind.* 45, 188-93T (1926).

necessary for heat to travel only a very short distance to the heat absorbing liquid. By removing the heat of reaction as latent heat of evaporation of some liquid boiling at the desired temperature and removing this heat by condensing the vapors through cooling with air or water or both, it was possible to insure a constant and uniform temperature for the full length of the catalyst zone as well. Of these two types the one in which the catalyst tube is completely surrounded by the boiling or heated liquid is the more efficient and has been adopted for large scale use. The entering
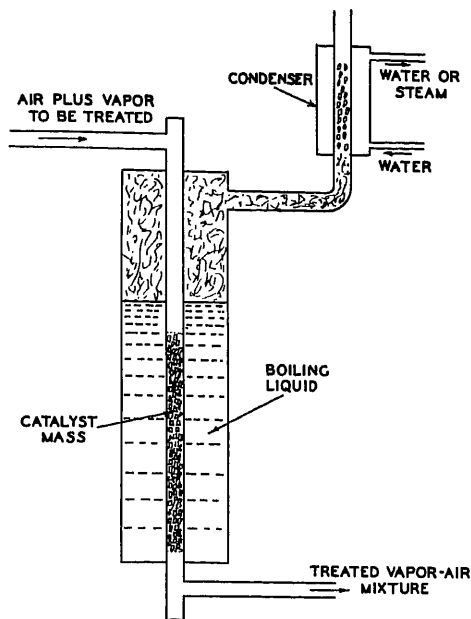
Fig. 52.—Apparatus for removal of reaction heat by boiling of a liquid.

gaseous mixture of air and hydrocarbon vapors first comes in direct heat transferring contact with the heated vapors of the boiling liquid and is thus preheated before reaching the active catalyst. Undue cooling of the forepart of the catalyst is thus avoided and reaction can occur even at this point.

In practice square catalyst tubes ⅝ to ¾ inches to the side are used. As each such tube would have a very small capacity, it is necessary that a number be used together in a commercial unit. For the vapor phase oxidation of naphthalene to phthalic anhydride, units consisting of over 1000 catalyst tubes, ¾ inch to the side and 36 inches long, and housed in a shell 36 inches in diameter are used. Square tubes are used for the catalyst as they present a larger surface to the cooling liquid per unit

volume than round tubes,[4] and also make possible the use of a smaller volume of boiling liquid since the square tubes may be fitted as near to each other as desired and may thereby be used to control the ratio of catalyst volume to boiling liquid volume. By welding the ends of the catalyst tubes together without using a tube sheet, it is possible to keep them very close together and to construct a converter requiring a minimum of liquid.
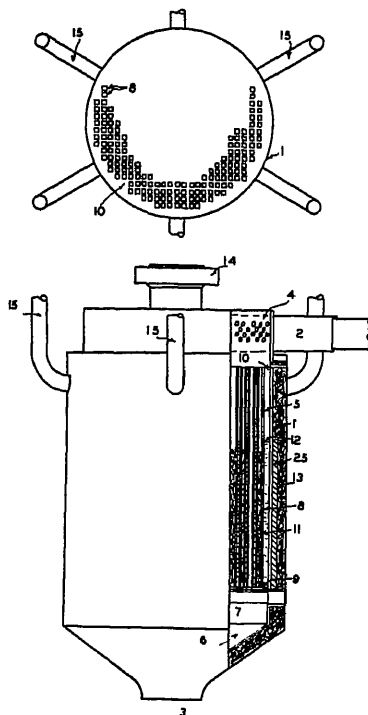
FIG. 53.—Mercury bath multiple tube catalytic oxidation apparatus (Downs).

Mercury has been proposed for use as the heat-removing liquid and is widely used for that purpose. Certain of its properties, such as boiling point, latent heat of vaporization, etc., make it a very desirable liquid to use, but it possesses the disadvantage of being heavy and expensive on a volume basis. Hence, apparatus designed for its use must require only the smallest possible amount for efficient operation.

Although the ratio of catalyst volume to mercury volume may be made quite small, as long as liquid mercury is kept in complete contact with the tubes in the catalyst zone, the ratio of catalyst volume to tube surface and the maximum distance of catalyst from tube surface must be controlled within limits. As the maximum distance which heat has to travel in passing from the reaction zone to the heat absorbing surface increases, the temperature differential or "driving force" between this maximum distance point and the absorbing surface must increase in order for the same amount of heat to be transferred. In this type of apparatus the rate at which heat reaches the tube wall controls the rate at which it may be dissipated by the mercury. Also it is imperative that the catalyst at no point exceed a definite maximum temperature, which depends in value upon the activity of the catalyst, to prevent undue losses by complete combustion. It is therefore necessary to restrict the cross sectional dimension of the catalyst tubes. The patent [4b] for the apparatus claims a minimum ratio of three square inches of tube surface per each cubic inch of catalyst volume. With square tubes ¾ inch inside

[4] a. U. S. Pats. 1,374,020-1 (1921) Downs assr. to the Barrett Co.; b. U. S. Pat. 1,604,739 (1926) Downs assrs. to the Barrett Co.

dimension this ratio is 4.35 square inches of surface per cubic inch of catalyst space. With smaller tubes the ratio increases and for a ⅝ inch inside square tube becomes 6.4. Conversely, as the tube cross section increases the ratio decreases and for a two inch inside square tube becomes equal to 2.0.

Such a catalytic converter with a two phase cooling medium can be made quite largely automatic in operation. Suitable condensing apparatus
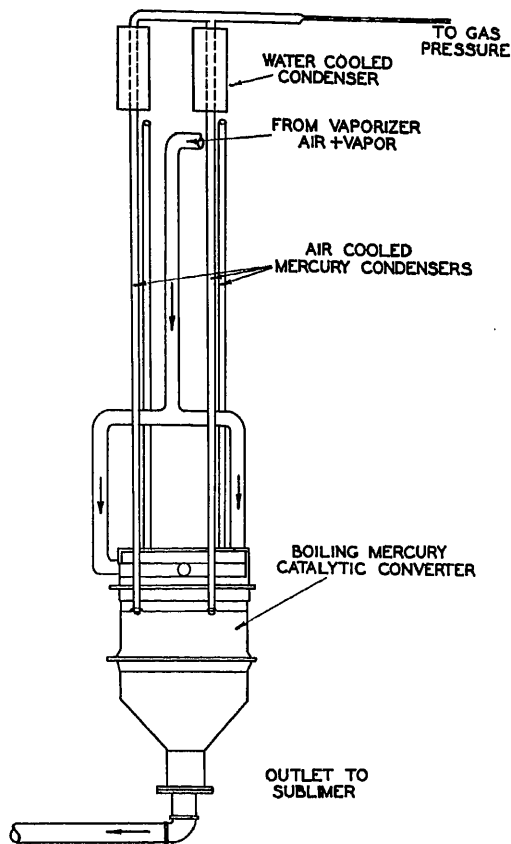
Fig. 54.—Simplified sketch of boiling mercury catalytic converter showing method for mercury condensation (Downs).

(*see* Fig. 54) returns the liquid that has been boiled away by reaction heat and the liquid reservoir is then constantly replenished. The vapor of the boiling liquid which surrounds the catalyst tubes serves as a transfer medium for carrying heat from the reaction to the cooling medium in the condensing system. Heat is thus removed without any change in temperature of catalyst.

This Downs type of mercury-controlled catalytic converter has been largely responsible for the expanded production of phthalic anhydride which has occurred since this country started making its own dye intermediates at the close of the war because of the operating economics made possible in the oxidation. A boiling mercury converter of approximately the same overall dimensions as the first-mentioned air-injector type has a capacity of from 1600 to 1800 pounds of phthalic anhydride per 24 hours and is so automatic in operation that a single operator can manage as many as eight of them.

The very large amount of heat removed in such a converter, which is about three feet in diameter and contains somewhat over 1000 catalyst tubes three feet long, may be calculated from the heat of oxidation of naphthalene. Although the heat of oxidation of naphthalene to phthalic anhydride is about 6000 B.t.u. per pound of naphthalene, the amount of concurrent total combustion which occurs in practice serves to bring this heat nearer to 10,000 B.t.u. per pound of naphthalene. On the basis of a 1600-pound-per-day production of phthalic anhydride about 21 million B.t.u. would be generated in each converter and removed by the boiling mercury and as sensible heat by the hot exit products.

Mercury as the heat-removing liquid possesses both advantages and disadvantages. The boiling point of mercury at atmospheric pressure is 357° C. but may be altered by increasing or decreasing the pressure on the system. For use in catalytic oxidations pressure must be maintained on the mercury system to raise the temperature of the boiling point to about 400° C. for operation with a fresh catalyst and possibly to as high as 450° C. for operation with a partly deteriorated catalyst. The ease and facility with which the boiling point temperature may be changed even while a converter is in operation is one of the special advantages possessed by mercury. However, the high toxicity of mercury vapor, and the difficulty of preventing leaks in a mercury vapor system under pressure operate as disadvantages. Also the mercury is heavy, expensive, has a relatively low rate of heat conductivity, and is subject to oxidation.

It should be stated, however, in defense of the mercury converter that these apparent difficulties have either been solved or have been found to be of little effect. Although considerable difficulty was experienced at first in the welded construction of the mercury converter due to leaks caused by improper construction or to strains produced by the expansion and contraction caused by uneven heating and cooling, this was soon solved. At the present time losses of mercury are negligible, possibly amounting to about 75 pounds per year from a converter holding 6000 pounds of mercury. Furthermore, although mercury has a rather high value per pound and still higher per unit of volume, due to its great weight, its salvage or recovery value is practically as high as the value of the original material. Usually a simple distillation is sufficient to restore it to its original purity. It does not decompose during use, does not react with

the steel apparatus, and does not oxidize when an inert gas such as carbon dioxide is used in the converter vapor space. On the other hand, the steel apparatus itself when ready for scrapping has only a very low junk steel value. Mercury does not wet the steel tubes and has a low thermal conductivity, but as it is in extremely violent ebullition during operation, the mixing thus obtained counteracts these apparent disadvantages. Also, the controlling factor in the rate of heat transfer is the rate at which heat can flow from the catalyst and hot gases to the confining tube wall, and not the rate at which it can flow from tube wall to mercury.

To eliminate the necessity for using mercury, other materials have been proposed as heat removing media. One of these is an alloy of cadmium and mercury.[5a, 6] Thus, by mixing cadmium which boils at 778° C. and mercury which boils at 357° C. alloys of different boiling points may be obtained. A mixture of 12 per cent (by weight) cadmium and 88 per cent of mercury, boils at 370° C.; at 40 to 60 mixture boils at approximately 430° C. If a reaction temperature of 425° C. in the catalyst mass is representative of optimum operating conditions, then a boiling temperature of 400° C. for the heat removing liquid is satisfactory. This allows a temperature difference of 25° C. as a "driving force." Such a boiling temperature is characteristic of a 25 per cent by weight cadmium —75 per cent by weight mercury alloy.

Data from the patent literature state that such a 25-75 mixture is liquid at 100° C., a valuable point since solidification is not likely to occur in the condenser or connecting lines if steam is used for condensation. The thermal conductivity of cadmium is higher than that of mercury and the density is lower.

Other alloys such as those composed of lead, tin, and mercury[6] have also been suggested. Thus, a mixture of 30 per cent by weight of lead, 30 per cent of tin and 40 per cent of mercury boils at 425° C. and may be used as a heat-removing and temperature-regulating bath.

Where the temperature of operation may require changing from day to day due to variation in catalyst activity, changes in raw material, or even the substitution of an entirely different material for oxidation, the atmospheric process of heat removal by a boiling mercury alloy does not give sufficient flexibility of temperature control. The pressure system employing only mercury as the liquid does permit changes in boiling temperature by alteration of the impressed pressure. By a combination of the two processes it is, of course, possible to increase the flexibility of temperature control of the alloy system by changing it in such a way that the pressure can be varied. It is likewise[7] possible to change the composition of the liquid bath by withdrawing condensed vapor, rich in mercury, from the condenser or by withdrawing liquid, rich in cadmium,

5 a. U. S. Pat. 1,689,860 (1929) Canon and Andrews assrs. to Selden Co.; b. Brit. Pat. 310,956 (1929) Jaeger assr. to Selden Co.
6 U. S. Pat. 1,735,951 (1929) Canon and Andrews assrs. to Selden Co.
7 U. S. Pat. 1,666,251 (1928) Andrews assr. to Selden Co.

from the bath. In this way the boiling temperature may be raised or lowered without the necessity for imposing pressure on the system.

Although the alloys and mercury amalgams have been stated to be cheaper than mercury alone on the basis of lower volume cost of lead, tin, cadmium, etc., their use has not been found to affect any saving in the cost of the product. The recovery of the materials in pure form is more difficult whenever changes in operation make such a step necessary, as far as is known. The various claimed advantages for such alloys and amalgams have not been substantiated and they have not been maintained in general industrial use for this purpose. Their use was broadly claimed in the Downs patent (Fig. 52) but only mercury has been found to give satisfactory operation.

Non-metallic substances such as sulfur have also been proposed for removing the heat of reaction from oxidation processes,[8] and have been used experimentally. Sulfur is superior to mercury in that it is much cheaper, much lighter, and can be more readily detected if leaks occur in the apparatus. The boiling point can be varied, as in the case of mercury, by changes in the superposed pressure. At atmospheric pressure sulfur boils at 444.6° C. or about 40° to 50° C. higher than satisfactory for use in controlling oxidation temperatures. For this reason sulfur must be used at reduced pressure in order that its boiling point may be sufficiently lowered. The apparatus may be made lighter in construction than when mercury under pressure is used.

Boiling organic compounds such as anthracene have been proposed and may be used. High speed forced circulation is required, however, to prevent overheating and the attendant decomposition and charring likely to be encountered. This necessarily complicates the operation and adds to the cost.

Excess heat may also be dissipated by the use of baths of fused salts, such as a mixture of sodium and potassium nitrates.[9a] Such a mixture, having a high thermal conductivity may also be used to maintain a uniform temperature along the catalyst tubes.

A type of catalytic converter designed to be used with fused salts of high thermal conductivity surrounding the catalyst tubes is shown in Figure 55.[9b] The mixture of air and hydrocarbon vapor to be oxidized is led through a centrally located, horizontal tube for the purpose of preheating and then through several, small, horizontal catalyst tubes. Both the central tube and the several catalyst tubes are immersed in the fluid bath which is maintained at the proper temperature. Heat generated in the catalyst tubes by the oxidation reaction is conducted away by the fluid and is removed as sensible heat in the reaction products which pass to a condenser and by radiation from the surface of the apparatus. Means for

[8] a. U. S. Pat. 1,589,632 (1926) Downs; b. U. S. Pat. 1,547,167 (1925) Downs.
[9] a. Brit. Pat. 275,321 (1927) Marks assr. to E. I. duPont de Nemours & Co., Inc.; b. U. S. Pat. 1,599,228 (1926) Gibbs assr. to E I. duPont de Nemours & Co., Inc.; Brit. Pat. 275,321 (1927) E. I. duPont de Nemours & Co., Inc.

heating the fluid by gas flames are provided for starting and for maintaining temperature when the heat losses by radiation are larger than the heat generated in the catalyst zone. Lead was used at one time and circulation in the bath was by convection currents only. However, heat transfer through the stagnant films near the confining walls would be low and mixing poor. Fused salts have been substituted for the molten lead as a heat-conducting medium.

The use of horizontal catalyst tubes in this type of apparatus entails somewhat more difficulty in the filling and emptying of catalyst than in
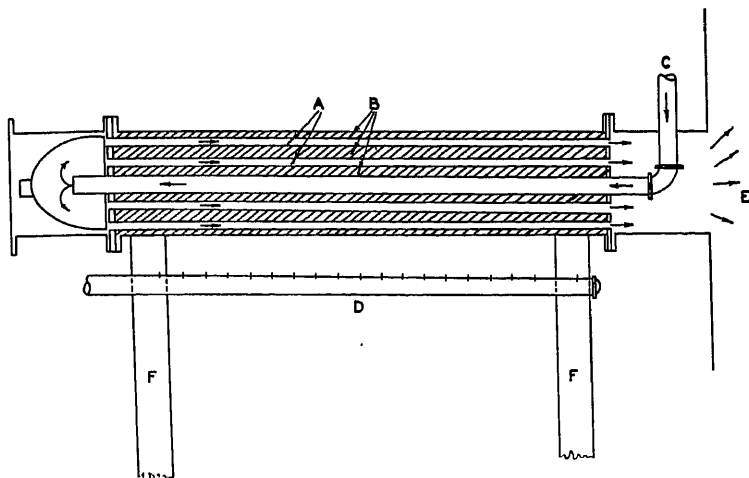
Fig. 55.—Catalytic converter employing fused salts as heat-conducting media (Gibbs)—not to scale.

A. Catalyst tubes partly filled with catalyst
B. Heat conducting medium
C. Inlet for air and vapors
D. Gas burner
E. Condenser
F. Supports

the vertical type of tubular apparatus. Also the catalyst tends to lie on the bottom of the tubes and to leave a free space on top. This is not ideal since it means channeling of the gases with resultant uneven heating and catalytic action. A vertical tube type of apparatus for the oxidation of naphthalene, etc., which employs fused salts rapidly circulated by a pump has been developed by the Monsanto Chemical Company and presumably eliminates some of the objectionable features of this apparatus. Details are not available for publication.

Although they have given successful performance, the boiling-mercury types of converters are unquestionably heavy and cumbersome, and are subject to some operational difficulties. Likewise, the circulated-liquid types are open to certain objections. In the case of the boiling-mercury

converters it should not be overlooked that due to the great density of the mercury the pressure is considerably greater and consequently the boiling point higher at the bottom than at the top of the mercury column. For every foot of increased depth of mercury the pressure at the bottom is increased by 12/29.9 or 0.401 of an atmosphere. Since the temperature of the boiling point of mercury is increasing at the rate of about 10° C. for an increase in pressure of 0.177 atmosphere in the region of the atmospheric boiling point, it is easy to see how any considerable depth of mercury bath would increase the boiling temperature at the bottom of the converter. Also, the efforts to economize on mercury and consequently on weight have led to greatly restricting the free spaces through which the mercury can circulate by convection currents. These factors together with the fact that in the downflow converters, extensively used, the most intense reaction may occur in the upper portions of the catalyst tubes have led to the many attempts made in an effort to improve the process.

Other types of apparatus have been designed to avoid the real and fancied disadvantages of weight, cost, toxicity, etc., of the mercury-controlled type. One of these combines the older tray-type principle with the tubular hot-exchange principle.[10] Catalyst layers arranged in annular shells permit closer temperature control by using the incoming cool gases to remove heat from the catalyst during the preheating operation.

The tubular converters using liquid metals as heat-removing media present such powerful heat-removing characteristics that it is possible to force them without danger of overheating. However, when reaction is forced the time of contact may not be sufficient to permit complete conversion to oxidized products. For such cases it has been suggested to use a second converter of the tray type and uncooled in which to allow the reaction to complete itself. The greater part of the oxidation is permitted to occur in the controlled reactor and small amount of oxidation that may yet occur presents no hazard of overheating in the second or even third converter.[11] This is true, however, only if the amount of oxygen is restricted because it must be remembered that phthalic anhydride will burn just as will naphthalene and unless precautions are taken large losses of raw material may occur if the catalyst temperature becomes too high.

This suggested type of operation resembles that used in the oxidation of sulfur dioxide to sulfur trioxide. In this inorganic reaction it is possible to use a high initial catalyst temperature to convert rapidly the bulk of the sulfur dioxide and then to finish at a lower catalyst temperature in order to get good conversion, because the reaction is reversible. Any dissociation of the sulfur trioxide that may occur at the high temperature may be overcome and reversed at a lower temperature more favorable to the desired equilibrium. The oxidation of organic compounds, such as

[10] U. S. Pat. 1,682,787 (1928) Jaeger assr. to Selden Co.
[11] U. S. Pat. 1,660,511 (1928) Jaeger assr. to Selden Co.

those being considered, is not a reversible reaction and advantage cannot be taken of the abnormally high rate favored by the higher temperatures with the expectation of reversing any damage done in the way of complete combustion.

Since the oxidized product in the great majority of the vapor phase catalytic processes is more stable to decomposition or further oxidation than the raw material at the start it is possible to employ recirculation of the reactant gases with intermediate cooling for purposes of control. The product may be completely or incompletely removed on each pass or may be permitted to accumulate as vapor in the circulated reaction gases.[12] While such recirculation and intermediate cooling may be depended upon to properly remove heat of reaction, it does not insure uniform or correct temperatures of the catalyst masses. For this purpose it is necessary to employ a special type of converter, Figure 56, which permits counter current heat exchange between incoming cool gases and hot catalyst in contact with hot reaction products. Non-boiling liquid baths may also be used in contact with the catalyst tubes to insure a more or less uniform temperature distribution from inlet to exit end of the catalyst length.

FIG. 56.—Catalytic oxidation apparatus employing recirculation of reaction gases.
1. Catalyst Chamber
2. Saturater
3. Heat Exchanger
4. Product Separator
5. Exit Gas Scrubber

In general, what has been said in regard to the oxidation of naphthalene to phthalic anhydride applies to the oxidation of benzene to maleic acid with the exception that the volume demand for phthalic anhydride is greater. Somewhat different methods are also used in the recovery of product due to its different nature.

Recent developments in the design of catalytic oxidation apparatus [12d] make use of a device whereby the reaction gases pass downward in direct heat exchanging relation with the inner wall of an annular catalyst tube, reverse, and pass upward through the annular catalyst mass. This tubular catalyst containing chamber is immersed in a liquid, heat removing medium. A large number of these catalyst tubes may be connected to appropriate

[12] a. Brit. Pats. 279,819 (1926), 300,968 (1927), 306,442 (1929), 306,519 (1929), 306,883-4 (1929) Jaeger assr. to Selden Co.; b. French Pats. 33,339 (1926) addn. to 626,491, 642,471 (1927), 665,264 (1928) the Selden Co.; c. U. S. Pat. 1,741,309 (1929) Jaeger assr. to Selden Co.; d. U. S. Pat. 1,826,548 (1931) Jaeger assr. to Selden Co.

inlet and outlet headers and the capacity of the apparatus adjusted by altering the number and size of the tubes.

Phthalic Anhydride

The gases leaving the catalytic converter at a temperature of about 400° C., in the case of naphthalene oxidation, first pass through a cooler consisting of a coil immersed in water. Here the pressure is reduced from about 15 pounds per square inch gage to atmospheric and the temperature lowered to a point just short of the dew point to prevent moisture condensation. Steam at a pressure of from 15 to 25 pounds per square inch gage is generated in the vapor cooler and used as process steam.

From this vapor cooler the vapors and gases pass to a condenser house where phthalic anhydride condenses out. The first section of this condenser house is insulated in such a way that crystallization of phthalic anhydride is slow and large, needle crystals result. Too rapid cooling at this point results in the formation of a large number of very fine crystals and the phthalic anhydride condenses into what is virtually a dust, difficult to recover. Although aluminum was first used in the construction of this condenser house, it has been found that steel construction is satisfactory. This house is made in sections each separated by baffle plates to make possible the separation of the product into different grades, the highest grade being the first to settle out and the worst contaminated grade the last. This house is built about 10 feet deep to permit easy raking out of the crystals at intervals during operation without the necessity for any operator to enter and without the necessity for shutting down.

After treatment to cause the polymerization of undesirable contaminants the high grade phthalic anhydride is vacuum distilled to yield the commercial product. This product is usually passed through a flake machine to produce phthalic anhydride flakes in which form about 80 per cent of the material is marketed. The flaked form has considerable advantage over the needle crystal form since its bulk density is much higher and any discoloration is more readily detected.

An 8- to 10-plate vacuum still constructed of heavy steel is used and operated under a vacuum of from 28 to 28.5 inches of mercury. Temperature control must be exact since too low a temperature results in the clogging of the product lines by the solidification of the phthalic anhydride and too high a temperature results in the distillation of product into the pumps. Automatic devices are used to insure proper operation at this point.

First quality needle crystals from the condenser are usually used without further purification or treatment in the manufacture of anthraquinone, etc., in the plant. Only the very dirty or badly contaminated product is sublimed and this is redistilled in vacuum columns after sublimation to insure a high-grade product.

Maleic Acid

In the production of maleic acid by the vapor phase catalytic oxidation of benzene the hot gaseous product coming from a converter similar to that used in naphthalene oxidation is first passed through a vapor cooler also similar to that used in the case of phthalic anhydride production. The gases and vapors then pass through an earthenware dip pipe into a tank of water where maleic acid dissolves. Two wooden tanks holding about 1000 gallons of water each are used in series, being switched back and forth as the solution becomes saturated and are drawn off for further processing. Wooden baffle plates are used and the solutions kept in violent agitation by the passage of the hot gases out of the distributor head on the earthenware pipe and through the solution. A silver metal coil cooler is used in each tank to prevent excessive temperatures from being attained. Only a small amount of heat must be removed since the gases are partially cooled before entering the absorber, and only a small cooling coil is required at this point.

This step in the process presents very severe corrosion conditions since the apparatus parts are subjected to the action of a hot, acid solution saturated with oxygen. Such materials of construction may only be used as will insure a satisfactory equipment life and a product free from contamination by corrosion products.

The 40-per cent acid solution obtained from the absorber may be decolorized by the use of decolorizing carbon containing no acid soluble ash, and maleic acid recovered by crystallization. Hard rubber lined pumps and aluminum lines are used and crystallization is carried out in enameled cast iron vats. Maleic acid is sold in the crystalline form although it is commercially obtainable in solution.

The solution of maleic acid after being decolorized may be used directly for the production of malic acid by hydrolysis, or of succinic acid by hydrogenation. To form malic acid the solution is heated in aluminum-bronze autoclaves. This alloy is not suitable for the absorber but may be used here due largely to the absence of oxygen. For small scale succinic acid production the electrolytic reduction method of Norris is more useful, but for large scale operation catalytic hydrogenation has been found to be desirable.

FLOW SHEET

Figure 57 shows a general layout for the phthalic anhydride process. Air compressed to 30 or 40 pounds per square inch gage is filtered and preheated, and then passed through the naphthalene vaporizer. The naphthalene vaporizer consists of a steam-jacketed pot fitted with baffle plates, a distributor for admitting the necessary air, and an outlet for the naphthalene-air mixture. No attempt is made to saturate the air with naphthalene at the temperature of the saturator, but steady conditions are maintained and secondary air is admitted to the stream before it enters the

catalytic converter in order to obtain the necessary excess air for conversion.

Air at the rate of 35 to 40 thousand cubic feet (room temperature) per hour and carrying the correct amount of naphthalene vapor from the vaporizer enters the catalytic converter from the top and passes downward through the thousand or more individual catalyst tubes. The entering air-vapor mixture first becomes preheated in passing through the empty upper portion of the tubes by the condensing mercury vapors until a temperature
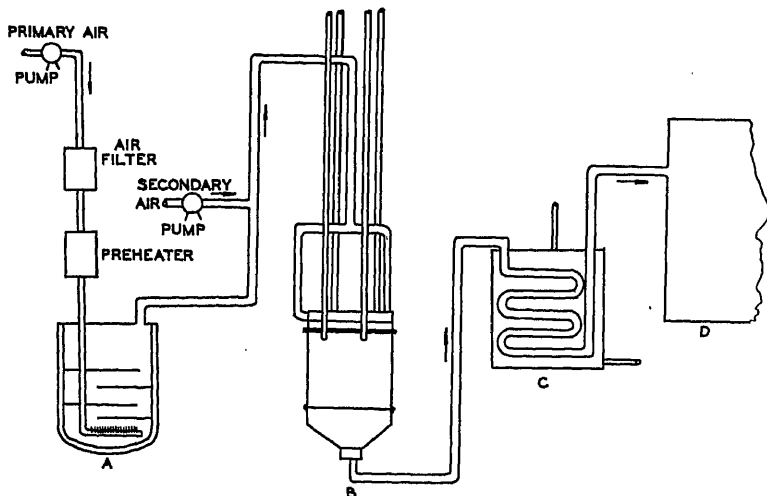
FIG. 57.—General layout for phthalic anhydride process.
A. Vaporizer for hydrocarbon
B. Catalytic converter for oxidation step
C. Cooler (dew point control)
D. Condenser for phthalic anhydride

near that for reaction is attained. The heated air-vapor mixture then passes through the catalyst in the tubes where the desired reaction occurs, the advantage of preheating being that practically all of the catalyst can be effective in promoting reaction. The reaction products pass out of the converter at the bottom and then into a vapor cooler and condenser house where phthalic anhydride is recovered.

Figure 58 shows a general layout for maleic acid production. A vaporizer is not used as in the case of naphthalene but a measured stream of benzene is fed into a stream of air under conditions that the benzene is vaporized and the correct air ratio for conversion is obtained. Secondary air may be used to correct the benzene-air ratio to the proper value. In practice benzene is fed to a coil immersed in hot water or steam, the benzene being measured by an orifice in small scale operation or by a proportioning pump in large scale operation.

From this point to product recovery the operation and the apparatus are the same as in naphthalene oxidation with the exception that a modified catalyst must be used for best results.

The principles made use of in the design of the catalytic oxidation apparatus described for use in phthalic anhydride and maleic acid production may be applied to the design of apparatus for the oxidation to partial oxidation products of anthracene, toluene, and other organic compounds derived from coal-tar, petroleum, and miscellaneous sources.
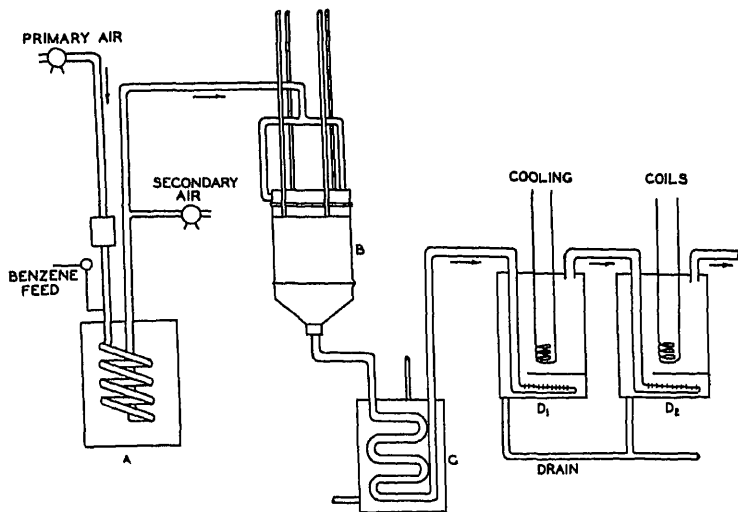
Fig. 58.- General layout for maleic acid production.
A, Vaporizing coil
B, Catalytic converter
C, Vapor cooler
D, *D₂*, Absorbers

Apparatus similar to that described and suitably modified to fit the characteristics of the reactants and products may be used with these other raw materials. In the product recovery and purification steps apparatus modifications will be more marked than in the actual oxidation step.

APPARATUS FOR THE OXIDATION OF PETROLEUM OILS

Figure 59 represents the type of apparatus used by James [18] for the oxidation of such petroleum fractions as kerosene, gas oil, or spindle oil. Before entering the catalyst chambers and before being mixed with any air the oil first passes through a Venturi meter for measurement and then through a tubular preheater, where the oil is completely vaporized and

[18] Bitler and James, *Trans. Am. Inst. Chem. Eng.* 20, 95-100 (1927).

superheated to 350° or 375° C. If heavy oils are being used, it is neces-
sary to complete the vaporization by admission of steam. From this
vaporizer the oil is passed to the oxidizing unit.

The hot oil vapors on entering the oxidizing unit are met by a stream
of air with which it thoroughly mixes before entering the catalyst screen.
The amount of air is so regulated that the vapors have a temperature of
about 410° C. immediately after passing the catalyst. Too high a pro-
portion of air results in the generation of excessive amounts of heat by
the reaction and causes the temperature to rise to such a point that large
losses to carbon dioxide may occur. The catalyst is of such a composition
that reaction may begin at as low a temperature as 250° C. but in practice
the reaction products are not cooled below 350° C. Cooling occurs by .
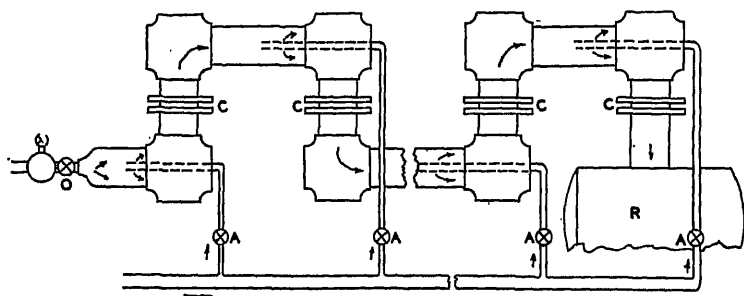
Fig. 59.—Type of apparatus used for oxidation of petroleum oils (James).
A. Air control valves
C. Catalyst screens
O. Oil control valve
R. Receiver

heat loss to the atmosphere from the surface of the apparatus between
successive catalyst screens, and to a certain extent by heating the fresh
air supplied between catalyst screens. Although cooling could be carried
farther from the standpoint of catalyst activity, condensation of the oil
and deposition of tars on the catalyst surface limits the temperatures that
may be used. As many catalyst screens as may be necessary to permit the
degree of oxidation desired in the product may be used in series.

The oil vapor and gases from the oxidizer pass to a tar separator
where the heavier portions of the product are allowed to collect before
the condenser is reached to prevent the formation of deposits in the con-
denser which would lower the thermal efficiency. A tubular condenser
with tubes and tube sheets of aluminum is used to collect the oil vapors
and oxidized products. The high proportions of organic acids in the
product make it essential that aluminum or other resistant metal be used
to prevent corrosion losses in equipment as well as contamination of
product. Because of the low concentration of product in the nitrogen gas
it is necessary to use a large condensing surface. A cooling surface of

about 330 sq. ft. is used with an oxidizer capable of handling 40 gallons of kerosene per hour.

The condensate then passes to a central receiving tank maintained at a 15 inch vacuum by suitable pumps, and is then ready for further treatment or fractionation prior to actual use. Water formed during the oxidation is separated from the oil in this receiving tank and is treated to recover dissolved oxidation products.

PRESSURE OXIDATION OF HYDROCARBONS

In the pressure oxidation of hydrocarbons it has been proposed [14] to saturate a portion of the hydrocarbon in liquid phase with oxygen by means of passing air countercurrently through the liquid under pressure. This oxygen containing part of the hydrocarbon is then to be brought into contact with the remainder of the hydrocarbon, which has been suitably preheated so that after mixing of the two streams, reaction temperature will be attained. The object of this method of introducing oxygen and of bringing the reaction mixture up to temperature is to minimize the hazard of explosion and to limit the extent of reaction by making possible very exact control of oxygen concentration and reaction temperature.

The oxygen concentration in the liquid hydrocarbon can be accurately controlled so that it does not exceed any predetermined value by providing adequate release valves in the compressed air line and at the bubble tower used for saturation. As long as the air pressure and hydrocarbon temperature at the saturator remain fixed, the extent of oxygen solubility is limited to a value that approaches equilibrium for the particular set of conditions.

By means of by-pass lines it is also possible to control accurately the temperature of the portion of the hydrocarbon that is subjected to direct heating. Then by suitably proportioning the amounts of the oxygen carrying stream to the heated stream, it is possible to introduce to the reaction chamber a definite amount of oxygen plus oil at a more or less definite temperature. As a further precaution against irregularities in operation it has been proposed to fit the reaction chamber with coils for heating or cooling. A layout of such an oxidation apparatus is shown in Figure 60.

The oxidized product is withdrawn continuously and cooled. Oxidized products may then be separated from the hydrocarbon, that has not been attacked, by washing countercurrently with aqueous methanol which is fed in at the top of a scrubbing tower. The oxidized products are selectively dissolved by the methanol solution which is heavier than and only slightly miscible with the hydrocarbon. A final washing of the hydrocarbon with water in the same way is used to remove any methanol taken up by the hydrocarbon and to assure as complete a removal of product as possible. The unoxidized hydrocarbon may then be recirculated and the products recovered by rectification of the methanol and water-wash solutions.

[14] Brit. Pat. 341,130 (1931) Standard Oil Development Co. Chapter VI, p. 200.

SOME FACTORS IN THE DESIGN OF HIGH PRESSURE EQUIPMENT

The tendency in recent years towards the use of high pressures in steam power plant operation, oil cracking, and numerous new synthetic processes which are dependent on high pressures for successful operation, has created a demand for high pressure equipment of all kinds. The development and use of this new equipment has not only contributed to our knowl-
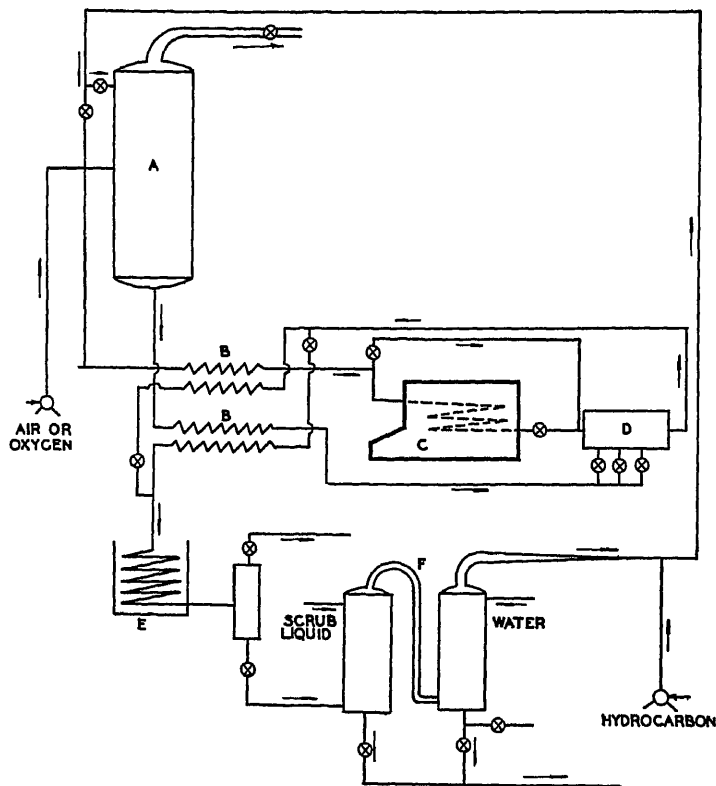
FIG. 60.—Layout of equipment proposed for the pressure oxidation of hydrocarbons.

A. Oxygen saturater
B. Preheaters
C. Furnace
D. High pressure reactor
E. Cooler and gas separator
F. Scrubbing system

edge of high pressure design but also has been responsible for the adaptation of a number of new alloys which are particularly well suited to withstand the severe conditions of operation frequently encountered in high pressure practice.

At present, considerable of the high pressure equipment may be considered standard and is readily available on the market. For instance, reaction chambers capable of withstanding high pressures and temperatures are now available in a variety of shapes and sizes and made in a variety of materials. Forged, cylindrical reaction chambers as large as ten by sixty feet have been fabricated. Gas compressors of the three or four stage type built by a number of manufacturers are capable of developing pressures up to 4000 pounds per square inch. Hyper compressors capable of developing pressures up to 1000 atmospheres are used in the synthesis of ammonia from hydrogen and nitrogen. Liquid pumps, from laboratory size up, are being manufactured to operate against pressures as high as 1000 atmospheres and in many cases are available in special alloys to handle corrosive materials. Gas and liquid storage cylinders are available in many sizes and for the entire pressure range covered by the commercial pumps and compressors. Valves, fittings, and tubing are made in a variety of sizes and of practically all of the special alloys, such as the chrom-nickel steels, stainless steels, special brasses and bronzes, monel metal, duralumin, etc.

In selecting a material for the construction of high pressure reactors a number of factors must be considered. The more important of these are as follows: 1, Ultimate tensile strength; 2, proportional limit; 3, corrosion resistance; 4, workability; 5, recrystallization if operating temperatures are to be as high as 500° C. or higher; 6, creep stress if the service period is to be long.

The ultimate tensile strength is ordinarily defined as the pull, expressed as pounds per square inch of initial area, required to break a standard test sample of the material. The proportional limit is that stress in tension above which the deformation is no longer proportional to the stress. In other words, if the proportional limit is exceeded, the material stretches abnormally. It is obvious then that the maximum working stress to which a material is subjected should always be less than is proportional limit under the conditions of operation. A convenient but arbitrary method of determining the maximum safe working stress for a given material consists in applying certain "factors of safety." For cold operation of steel (under 300° C.) a safety factor of about 3 is usually adequate. The working stress is calculated by simply dividing the ultimate tensile strength of the steel at 300° C. by the factor 3. For temperatures from 300° C. to 600° C. a safety factor of 5 should be used with most steels. The working stresses calculated with these safety factors will be found to fall within the proportional limit almost without exception. For temperatures above 600° C. which are advisable only with certain alloys, the working stress should preferably be determined directly from a plot of proportional limit over this range. Usually a value of about 75 per cent of the proportional limit will be satisfactory. In case length of service becomes a factor the

"creep stress" of the material should be taken into consideration as mentioned below.

It should be noted that the factors of safety mentioned above are not applicable in general to all materials at these temperatures but are chosen with reference to steel and its alloys only. A material such as duralumin, for instance, has a tensile strength at room temperature which compares favorably with that of steel. This aluminum alloy is weakened by an increase in temperature to a much greater degree than steel, however. For high pressure work, duralumin has little value at temperatures above 250° to 300° C.

Problems of surface corrosion in high pressure work do not differ materially from similar problems encountered in low pressure work. There is, however, one type of corrosion encountered in some high pressure processes which occasionally is a source of trouble. It has been found that hydrogen at high pressure diffuses quite readily through ordinary carbon steel at about 500° C. In passing through the steel the hydrogen reacts with the carbon in the steel. Since the tensile strength of a carbon steel is almost directly proportional to the amount of carbon present over the usual range, it is apparent that the removal of carbon will weaken the steel. In addition, a change occurs at the crystalline boundaries due probably to the combined effect of temperature and carbon removal, such that the steel is weakened still further. Corrosion of this type can be avoided by lining the reactor with some material, such as copper for instance, through which the hydrogen does not diffuse at an appreciable rate. A number of the steel alloys recently developed, particularly the chrome-nickel alloys, show excellent resistance to the action of hydrogen.

The workability of a material may or may not enter as an important factor depending entirely on the amount of manipulation and machining that is required in any particular case. Since practically very little high pressure equipment has yet reached the stage of quantity production, the workability of the stock can usually be neglected.

Some alloys of steel when operated for long periods at high temperatures are subject to recrystallization with an increase in crystal size. This crystal growth results in a weaker structure which under continued service may eventually result in failure. Several alloys have been developed, however, in which the rate of crystal growth is very small.

Under the discussion of proportional limit above, mention was made of "creep stress" of a material as a factor in design for long service periods. Recent tests have shown that at high temperatures the continuous application of a stress even lower than the proportional limit stress will cause progressive elongation of a piece with eventual failure. Data are now available for many of the so-called "high temperature alloys" giving the creep stress at various temperatures. This stress usually denotes the continuous pull in pounds per square inch which gives a certain per cent elongation in a given period of time. Where length of service is

an important item the "creep stress" must be taken into consideration in calculating the maximum working stress allowable.

A number of formulas have been developed for calculating the stress in thick walled cylinders due to internal pressure. From Barlow's formula:

$$P = \frac{2ts}{D}$$

in which

$P =$ internal pressure in lbs./sq. in.
$s =$ average stress in lbs./sq. in.
$t =$ wall thickness
$D =$ internal diameter of tube.

Similar formulas of Clavarino and Hütte have been set up graphically such that the ratio of wall thickness to internal radius or diameter can be read off directly.[15]

In the operation of large scale equipment, the most important single problem is the control of temperature by regulation of heat flow. This is not true of small scale, laboratory apparatus where the surface to volume ratios are much larger than in industrial apparatus.

Indirect, coil cooling is not generally applicable because of the danger of overcooling. The problem with most catalytic reactions is the removal of heat at a high temperature and not cooling, as such. Special means must be used, particularly where pressures and temperatures are high. Some of these are:

1. By use of a combination heat exchanger and reactor. By an arrangement of baffle tubes in a reactor the cold feed gases are preheated and the products partly cooled. Heat of reaction is removed as sensible heat in the product and partly by heat losses from the reactor wall.

2. A less desirable method of accomplishing the same end is to allow the cold, feed gas to mix with the hot product.

3. A method that is almost always used is to limit the extent of reaction to a point where heat losses equal heat of reaction, and recycle unreacted material.

4. A method similar to (3) is to use a series of reactors with intercooling and separation of product.

5. A diluent material may be added to the reactants to remove reaction heat as sensible heat. Gases cannot very well be used for this purpose since they defeat the purpose of pressure by reducing the partial pressure of the reactants. In the hydrogenation of oils, a surplus of oil serves as a diluent.

6. As is done in the case of the atmospheric pressure, catalytic oxidation of naphthalene to phthalic anhydride, a liquid boiling at the reaction temperature may be used to remove reaction heat as latent heat.

In the case of an endothermic reaction where it is necessary that heat

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[15] Marks, "Mechanical Engineers Handbook," New York, McGraw-Hill Book Co., Inc.

be added, a coil type of heater—developed and widely used in petroleum cracking—may be used to heat the reactants after compression but prior to entering the reactor. Heat is almost never added to reacting materials through the walls of the high pressure reaction chamber since the extra strain caused by the high surface temperatures rapidly reduces the life of equipment. Internal electric heaters have been used in certain special cases where it is necessary to apply heat to the interior of large apparatus. To prevent overheating of substances which are subject to injury by excessive temperatures, heating by means of the vapors of high boiling substances may be used. For instance, lubricating oils are being heated for distillation by means of mercury vapor. Vapors of diphenyl, diphenyl oxide, and similar substances are also well suited to this use. The heat of condensation of steam becomes small at high temperatures and pressures and steam is not well suited for heating to high temperatures.

Apparatus for the Oxidation of Methanol to Formaldehyde

The general type of apparatus used by Orloff for the oxidation of methanol to formaldehyde has been most widely publicized. It consisted of (1) a methanol vaporizer in which methanol was vaporized into the air stream at a controlled concentration, (2) a catalytic chamber where the oxidation took place, and (3) a recovery system for separation of the product into fixed gases, formaldehyde solution, water, and unreacted methanol.

One form of the catalyst chamber consisted [10] of a nest of 169 copper tubes 19 mm. in diameter by 800 mm. long arranged in concentric circles and held in a horizontal position. Each copper tube had a glass tube 300 mm. long placed in it; and in each glass tube a roll of freshly reduced copper gauze 12 mm. long (15×15 wires per sq. cm.) was mounted. To start the oxidation this bundle of catalyst tubes was heated to 300° C. and the mixture of methanol vapor and air passed in. The heat of reaction was sufficient to maintain the temperature at the desired point. A unit apparatus of the early type had a capacity of 170 to 176 Kgm. (about 79 pounds) of methanol per 10 hours of operation.

A modification of this type of catalyst chamber is that known as the Meyer apparatus. The principal difference between the two forms is that the Meyer uses a smaller number of larger tubes for the catalyst. Six copper tubes about 600 mm. long and 50 mm. in diameter are used and contain the catalyst which consists of rolls of copper gauze 110 mm. long.

In both of these types of equipment heat removal is by radiation and in the form of sensible heat in the reaction products.

[10] Ullmann, "Enzyklopädie der technischen Chemie" (1917), p. 576.

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